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26-Ring-Channel Structure Constructed from Bimetal Phosphite Helical Chains

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Since the preparation of the $AlPO_4$ family[1] with zeolite structures and the discovery of 14.1 Å channel in mineral cacoxenite[2] were reported, the synthesis of inorganic open frameworks with extralarge channels has been intensively studied in the systems of silicates, germinates, and metal phosphates.[3−21] With larger pores or channels in structure, more applications may be realized to meet the increasing demand on advanced materials for performing shape-selective catalysis on reactants too large to enter the pores of currently employed industrial catalysts, designing low-k materials and MRI contrast reagents[22] as well as gas storage materials with extraordinarily high capacity.[23] Recent discovery on the novel photoluminescence property of microporous structures has also extended their use from molecular sieve to inorganic phosphor as a new class of intrinsic luminescence materials.[19,20]

It is a highly challenging task to design an inorganic structure with a desired pore size, since metal−oxygen building units can exist in various geometric polyhedra and display an assorted connectivity. Thus, unlike MOF,[24] designed synthesis in microporous inorganic materials cannot be easily achieved. To our knowledge, the largest channel size ever reported in them is 24-membered rings (24R) which was only discovered in three germinates[6−8] and six MPO compounds.[13−17,21] Navigating through the periodic table, however, one can find nearly forty metal elements to form M−O−P bonded open frameworks, but only three of them, that is, M = Ni, Zn, and Ga, were observed to create 24R channel structures. Yet all synthetic MPO frameworks have not attained a channel size large enough to be compared with that of the naturally formed channels in cacoxenite which contains both Al and Fe metal centers. In contrast, existing 24R channel structures are only constructed from one kind of the polyhedral metal centers, for example, tetrahedral Zn^{2+} in ND-1 or ZnHPO-CJ1, tetrahedral Ga^{3+} in NTHU-1, and octahedral Ni^{2+} in VSB-1 or VSB-5. Inspired by nature cacoxenite, we have started to exploit bimetal systems aimed at creating aluminum-containing open frameworks and discovered a novel bimetal phosphite structure with 26R channel, $(C_4H_9NH_3)_2[AlFZn_2(HPO_3)_4]$ (designated as NTHU-5). This finding pushes the existing maximum channel size from 24R forward up to 26R (Figure 1).

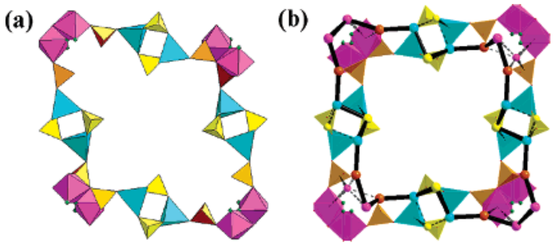

Figure 1. The 26R unit in NTHU-5: (a) each ring is composed of six AlF_2O_4 octahedra (purple), eight ZnO_4 tetrahedra (cyan), and twelve HPO_3 groups (yellow/orange); (b) the overlap of two consecutive 4_2-symmetry-related 26Rs with the top one (same as plot a) being drawn in ball-and-stick model for a clear view of the connection.

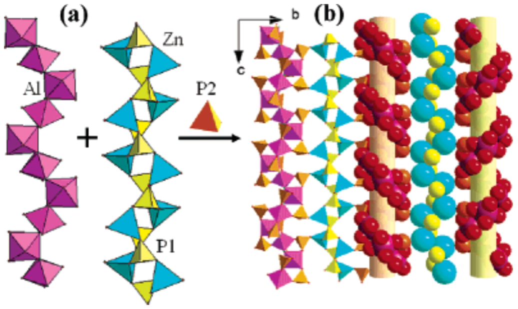

Figure 2. Two types of helical chains in NTHU-5: (a) ${}_{\infty}[AlFO_4]$ helix (left) and ${}_{\infty}[Zn(HPO_3)]$ chain (right); (b) section of interlinked helical chains through $HP(2)O_3$ units. In this plot, the space-filling model is drawn to emphasize their helical nature.

NTHU-5 was prepared by heating a mixture of Al_2O_3, $Zn(NO_3)_2$, HF, H_3PO_3, $C_4H_9NH_2$, C_2H_5OH, and H_2O in the molar ratio of 1:1: 4.5:6:10:106:666 in a Teflon-lined acid digestion bomb at 120 °C for 2 days under autogenous pressure. The resulting product consisted of a single-phased NTHU-5 in a yield of 66% (based on the limiting reagent zinc). Single-crystal structure analysis[25] revealed that the three-dimensional inorganic framework is built up with octahedral AlF_2O_4, tetrahedral ZnO_4, and two HPO_3 units, which form two types of helical chains along the *c*-axis (Figure 2). One of the helical chains is the neutral 4R chain of ${}_{\infty}[Zn(HPO_3)]$ with $HP(1)O_3$ units being located in the chain center and ZnO_4 tetrahedra on two sides for outward connection (Figure 2a), in contrast to common 4R chains with ZnO_4 tetrahedra in the chain center with phosphite/phosphate groups outward.[26] The other helical chain is the negatively charged ${}_{\infty}[AlF(HPO_3)_2]^{2-}$, which contains a ${}_{\infty}[AlFO_4]$ helix as the chain axis with $HP(2)O_3$ groups surrounding the axis and acting as linkers to connect with ${}_{\infty}[Zn(HPO_3)]$ chains (Figure 2b). Therefore each ${}_{\infty}[Zn(HPO_3)]$ chain is connected to two ${}_{\infty}[AlF(HPO_3)_2]^{2-}$ chains while each ${}_{\infty}[AlF(HPO_3)_2]^{2-}$ chain is connected to four ${}_{\infty}[Zn(HPO_3)]$ chains resulting in the unprecedented 26R tunnels in microporous materials (Figure 3).

The most striking feature of NTHU-5 is that every channel is constructed by a concatenation of 26R units (Figure 1a) which are interlinked through Al−F−Al and P−O−Zn bonds. The 26R unit is composed of six AlF_2O_4 octahedra, eight ZnO_4 tetrahedra and twelve HPO_3 groups. Every two consecutive 26Rs along the channel direction are 4_2-symmetry-related (Figure 1b), and the square channel openings observed on *ab* plane are the overlap of 26-membered rings. Maximum free atom-to-atom distance across the ring is 20.1 Å and the solvent accessible volume within the structure was estimated as 52.1% of the unit cell.[27] Butyl ammonium ions are located within channels with terminal $-NH_3^+$ groups

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10.1021/ja070733k CCC: $37.00 © 2007 American Chemical Society

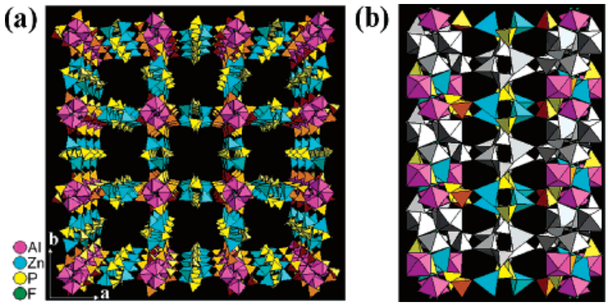

Figure 3. The structure of NTHU-5: (a) perspective view along the *c*-axis, showing 26R channels encircled by helical chains (organic cations are omitted in the plot); (b) side view of one 26R channel showing lateral 8R windows. The channel is also composed of a stack of 26-membered rings which are shown in alternating gray and colored polyhedra.

orienting toward the charged helical $_\infty[AlF(HPO_3)_2]^{2-}$ chains at four corners. They also form hydrogen bonds with the neutral $_\infty[Zn(HPO_3)]$ chains on four edges (Figure S4). The existence of this organic component was confirmed by both ^{1}H MAS NMR data and elemental analysis.[28]

NTHU-5 has been considered to be the first 26R channel structure ever reported. It is also for the first time that a microporous structure with participation of aluminum in a pore size over 20R is prepared. All Al^{3+} centers are difluorinated with two μ_2-F ligands forming one octahedral edge. The presence of fluoride was confirmed by ^{19}F NMR spectroscopy. We also measured the ^{27}Al MAS NMR spectrum which showed one distinct resonance at −11.8 ppm, indicating that the chemical shift of octahedral Al^{3+} in phosphite lattice is fairly close to that in phosphate lattices.[29] Moreover, ^{31}P solid-state NMR data revealed two resonances with chemical shifts at 6.0 and −0.4 ppm. They respectively correspond to P(1) and P(2) for $HP(1)O_3$, connected with three Zn centers, and $HP(2)O_3$, connected with one Zn and two Al centers. The phosphite hydrogen was confirmed by its characteristic P−H stretching at 2395 cm^{-1}, and its ^{1}H resonance was observed at a chemical shift of 7.5 ppm (Figure S7).

The bimetal-containing NTHU-5 structure can sustain heat up to 210 °C, being more stable than the single metal 24R structure of ZnHPO-CJ1.[21] These two compounds have the same M/P ratio of 3:4 and the same organic cations, but they adopt entirely different structures. The compositional difference lies in the differently charged heterometal atom Al, which is also fluorinated and no longer four-coordinated as Zn. From the view of synthesis, NTHU-5 may be considered as a thermodynamically and kinetically stable phase. Compared with existing 24R channel structures, NTHU-5 was actually prepared at the lowest temperature with the shortest reaction time and could be easily reproduced in single crystalline phase with a reasonably high yield. Furthermore, we discovered that the trivalent metal site in NTHU-5 could be replaced by heterometal other than Al. If $M(NO_3)_3$ (M = Ga or Fe) is used in place of Al_2O_3 in the above synthesis, Ga or Fe analogue of NTHU-5 can be obtained as a nearly pure-phase product in high yield as well (see Table S1). In the Ga analogue, it is the GaF_2O_4 octahedra that forms a $_\infty[GaFO_4]$ helical chain axis via the bridging of μ_2-F. We found that the ^{31}P resonance for P(1) remained a chemical shift at 6.0 ppm but P(2) was down-shifted to 3.7 ppm owing to the P−O−Ga linkage. In the Fe analogue, the octahedral helix becomes $_\infty[FeFO_4]$, which renders magnetic property to the NTHU-5 structure (Figure S11).

This study has demonstrated that differently charged metal ions can together form M−O−P−O−M′ bonded structure with ring size larger than any other existing inorganic open frameworks. The unique structure of NTHU-5 is built with two types of helical chains with its unprecedented 26R channel being truly a stack of 26-membered rings instead of just an opening. In addition to Al^{3+}, other trivalent metals with adequate crystal radii and six-coordination, for example, Ga^{3+} and Fe^{3+}, can be adopted by NTHU-5.[28] This is an extraordinary property since previous examples showed that intraframework metal sites could only be partially doped, otherwise they may result in structure variation. The system of NTHU-5 has provided an intriguingly new chemical synthesis for inorganic microporous materials with optimal reaction conditions. Further research on this system is in progress.

Acknowledgment. We are grateful to National Science Council (Grants NSC-95-2119-M007-016 and NSC-95-2113-M008-009-MY3) for financial support.

Supporting Information Available: Crystal data, structure plots, results from ICP−AES, EA, TGA, NMR, IR, PL, and magnetic study and crystallographic CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA070733K