$[Ga_2(DETA)(PO_4)_2]\cdot 2H_2O$ (DETA = Diethylenetriamine): A Novel Porous Gallium Phosphate Containing 24-Ring Channels

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The synthesis of microporous metal phosphates has been an area of intense research due to their rich structural chemistry and potential applications in catalysis, separation, and ion-exchange processes.[1] One of the main goals of this research is to synthesize zeolite-like materials with large ring sizes so that one can perform shape-selective catalysis on reactants too large to enter the pores of currently employed industrial catalysts. In 1988, Davis et al. reported a material called VPI-5 that contained an 18-membered ring.[2] It was not until 1991 that a gallophosphate with gigantic pores of 20-ring was prepared, namely, cloverite.[3] Recently, the pore size has been extended to 24-membered ring in the transition metal phosphates, that is, ND-1[4] and VSB-1.[5] These materials have set the stage for the development of other extra-large pore, crystalline molecular sieves. In contrast, the largest pore ever discovered among the phosphates of group 13 elements has only 20-membered rings and exists in three materials: cloverite, JDF-20,[6] and $[NH_3(CH_2)_4NH_3]_2[Ga_4(OH)_3(PO_4)_3(HPO_4)_2]\cdot xH_2O$.[7] Attempts to prepare materials with even wider pores have produced a novel gallophosphate, $[Ga_2(DETA)(PO_4)_2]\cdot 2H_2O$ (DETA = diethylenetriamine) (referred to as NTHU-1), whose neutral framework consists of channels made of 24-membered rings. DETA binds in a tridentate fashion to half of the Ga centers within the framework. The incorporation of divalent heteroatoms into the framework of NTHU-1 was also explored. Here we report the synthesis, crystal structures, and some preliminary findings on the physical properties of NTHU-1 and the cobalt- and manganese-substituted compounds.

NTHU-1 was prepared by heating a mixture of Ga_2O_3, diethylenetriamine, H_3PO_4, H_2O, and ethylene glycol in the molar ratio of 0.5:5.1:6:333:110 in a Teflon-lined acid digestion bomb at 180 °C for 3 days under autogenous pressure followed by slow cooling at 6 °C h^{-1} to room temperature. The resulting product consists of colorless cubic crystals of NTHU-1 in a yield of 53% along with a small amount of unknown colorless powder. The powder can be easily removed with the aid of an ultrasonic vibrator. A suitable crystal was selected for structure determination by single-crystal X-ray diffraction. Elemental analysis confirmed its stoichiometry. Anal. Found: C, 10.55; H, 3.68; N, 8.68%. Calcd: C, 10.25; H, 3.66; N, 8.97%. The cobalt- or manganese-substituted NTHU-1 were prepared by heating Ga_2O_3, CoO, or $MnCl_2\cdot 4H_2O$, diethylenetriamine, H_3PO_4, H_2O, and ethylene glycol in the molar ratio of 0.4:0.2:5.1:6:333:110 under the same hydrothermal conditions. Energy-dispersive X-ray fluorescence spectroscopy confirmed the presence of Co and Mn in the blue and colorless cubic crystals, respectively.

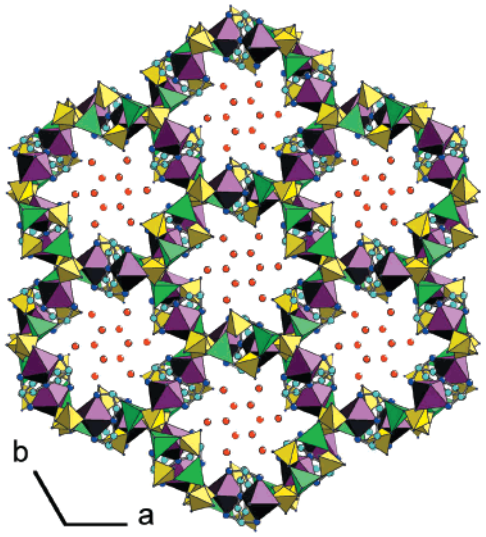

Figure 1. Perspective view of the structure of NTHU-1 along the *c*-axis, showing nanochannels filled with water molecules (red solid circles). The GaO_4 tetrahedra are indicated in green, GaO_3N_3 octahedra in purple-red, and PO_4 tetrahedra in yellow. The DETA ligands are represented in ball-and-stick model (N, blue; C, cyan). The H atoms are omitted for clarity.

The compound was characterized by single-crystal X-ray diffraction.[8] Its three-dimensional framework structure consists of close-packed channels in hexagonal, honeycomb arrays, which are oriented parallel to the *c*-axis (Figure 1). There are two distinct channel water molecules per $[Ga_2(DETA)(PO_4)_2]$ unit, a number that is also consistent with the result from thermal gravimetric analysis (TGA). One of the lattice water molecules is hydrogen-bonded to the uncoordinated oxygen of $P(1)O_4$ group as inferred from the short O(4)···O(10) distance of 2.54 Å. The walls of the channels are made of corner-sharing $Ga(1)O_4$ tetrahedra, $Ga(2)O_3N_3$ octahedra, and PO_4 tetrahedra (Figure 2). DETA binds to Ga(2) as a terminal tridentate ligand. A short P(1)−O bond is directed toward the channel space with the oxygen being uncoordinated. Polyhedral bond distance averages are Ga(1)−O 1.834, Ga(2)−O 1.948, Ga(2)−N 2.065, P(1)−O 1.538, and P(2)−O 1.534 Å. Within the unidimensional channels are puckered 24-ring windows formed by the edges of 12 GaO_4 tetrahedra and 12 PO_4 tetrahedra in an alternating manner (Figure 3), making one of the largest crystalline pore GaPOs known to date. The shortest O···O atom-to-atom distance across the 24-membered ring is 10.4 Å. Adjacent 24-membered rings are linked to form channels via $Ga(2)O_3N_3$ octahedra and $P(2)O_4$ tetrahedra. The position of the bonded amine molecule causes the shape of the channel to be hexagram. Each channel contains six lateral elliptical 12-ring windows delimited by two GaO_3N_3 octahedra, four GaO_4 tetrahedra, and six PO_4 tetrahedra, through which they

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(8) Crystal structure data for NTHU-1 ($[Ga_2(DETA)(PO_4)_2]\cdot 2H_2O$). Unit cell: $a = 23.781(1)$ Å, $c = 13.466(1)$ Å, $V = 6595.2(8)$ Å^3 at $T = 296$ K, $Z = 18$, trigonal space group *R-3* (No. 148), $\rho_{calcd} = 2.124$ g cm^{-3}. 14475 reflections collected ($2\theta_{max} = 56.6°$, $\lambda = 0.71073$ Å), 3593 unique, 2992 observed ($I_o > 3\sigma(I_o)$). Final refinement (191 least-squares parameters) converged to $R_1 = 0.0264$, $wR_2(F^2) = 0.0844$, GOF = 1.017.

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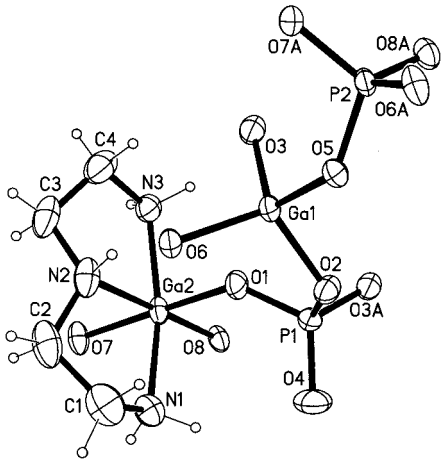

Figure 2. Local coordination of the NTHU-1 framework atoms showing the atom-labeling scheme and ellipsoids at 50% probability. Average bond distances: Ga(1)−O = 1.834(2) Å, Ga(2)−O = 1.948(2) Å, Ga(2)−O = 1.948(2) Å, Ga(2)−N = 2.065(3) Å.

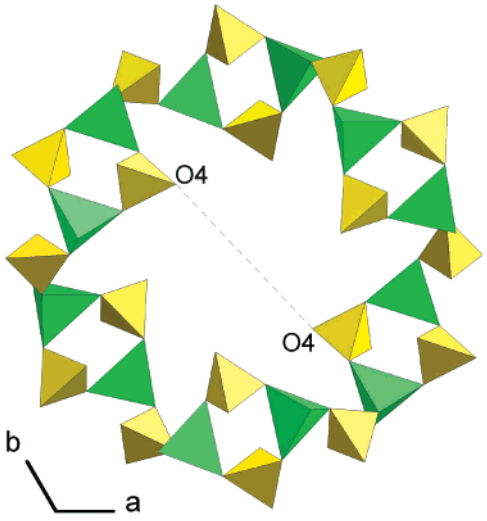

Figure 3. Polyhedral plot of the puckered 24-membered ring formed of 12 GaO_4 (green) and 12 PO_4 tetrahedra (yellow). View perpendicular to the plane of the ring. The dashed line connects the two O atoms with the shortest distance across the 24-ring.

connect neighboring channels. For NTHU-1, the framework metal atom density is 10.9 M atoms (M = Ga, P) per 1000 Å^3, compared with the value of 12.7 for faujasite,[9] 12.1 for ND-1 and the iron phosphate mineral cacoxenite,[10] 11.2 for JDF-20, 11.1 for cloverite, 10.5 for ASFe-1,[7] 10.1 for $N(CH_3)_4ZnH_3(PO_4)_2$,[11] and 9.3 for $[HN(CH_2CH_2)_3NH]K_{1.35}[V_5O_9(PO_4)_2]\cdot xH_2O$ which is among the lowest framework density materials known.[12] The presence of large pore openings about 11 Å in NTHU-1 is confirmed by BET measurements.[13]

Dehydration of NTHU-1 can be achieved by heating to 120 °C in air, but the sample rehydrates on exposure to air. TGA results showed weight loss of 7.3% from 25 to 120 °C (−2 H_2O) and thermal stability from 120 to 300 °C. Further heating to 1150 °C resulted in $GaPO_4$ and black glassy carbon as the final products, as indicated from powder X-ray diffraction and the color. To determine the thermal stability of NTHU-1, a single crystal was heated to 250 °C, kept there for 5 h, and cooled to room temperature. Single-crystal X-ray diffraction study on the crystal indicates that the structure of NTHU-1 is clearly sustained.

We have also synthesized metal-substituted NTHU-1 incorporating the divalent metals Co and Mn. Energy-dispersive X-ray fluorescence spectroscopy confirmed the presence of Co or Mn in the crystals. Both compounds have unit-cell dimensions similar to those for NTHU-1, and their structures have been determined by single-crystal X-ray diffraction. They adopt the NTHU-1 structure. Least-squares refinement results suggest that both cobalt and manganese ions substitute for the four-coordinated gallium centers up to 10%, that is, the metal sites are best modeled as having 10% Co or Mn and 90% Ga occupancy at the tetrahedral Ga(1) site and 100% Ga occupancy at the octahedral Ga(2) site. Electron-probe microanalysis on a blue crystal of cobalt-substituted NTHU-1 indicates the presence of 5.0% cobalt, which is consistent with the results from X-ray diffraction. Presumably the uncoordinated oxygen of $P(1)O_4$ group is protonated to balance the charge. The cobalt- or manganese-substituted NTHU-1 is expected to show high acidity, which, in combination with redox-active transition metal, could lead to possible catalytic activity.

To our knowledge, all microporous phosphate materials with ring sizes over 20 consist of anionic frameworks. For example, the anionic frameworks of ND-1 and VSB-1 consist of one-dimensional channels filled with amine cations. In contrast, the framework of NTHU-1 is neutral and does not contain cationic templates in the channels. Unlike other metal phosphates, NTHU-1 consists of the organic amine DETA as a tridentate ligand within the framework rather than as a countercation. Several metal phosphates containing triprotonated DETA as a template were reported.[14−16] NTHU-1 provides an interesting example of the use of multidentate organic ligand in generating novel mixed organic−inorganic frameworks. The replacement of DETA by other ligands such as the extended analogue dipropylenetriamine or the chelate *o*-phenylenediamine in the hydrothermal synthesis may result in novel porous structures. Further research on this theme is in progress.

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Supporting Information Available: TGA and DTA curves, powder X-ray diffraction patterns of NTHU-1 before and after thermal treatments, Horvath−Kawazoe differential pore volume plot, tables of crystal data and refinement, atomic coordinates, thermal parameters, and bond distances and bond angles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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