

## Zinc Phosphate with Gigantic Pores of 24 Tetrahedra

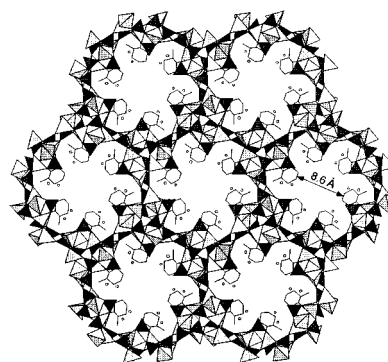
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Materials with open-framework structures are of great importance in many fields of today's applied chemistry, such as ion-exchange, molecular sieving, catalysis, etc.<sup>1–3</sup> The search for new phosphate and other materials with open-framework structures with increasingly larger cavities has been extremely intensive in recent years.<sup>4,5</sup> The number of new synthetically made compounds with extralarge pores, i.e., pores of more than 12 tetrahedra, has grown steadily since 1988, when VPI-5 with 18-membered rings was discovered.<sup>4,6</sup> The largest openings known so far among the silicates and phosphates are of 20-membered rings, for two synthetic phosphates, cloverite and JDF-20,<sup>7,8</sup> and one natural phosphate, cacoxenite.<sup>9</sup> Different approaches toward the synthesis of such materials have been suggested and studied in the past. Among those are, for example, the use of large or oligomeric templates as well as the selection of framework elements that can form three-membered rings such as the zincosilicates and the zincophosphates,<sup>4</sup> or synthesis of nonoxide-based materials.<sup>5</sup> Yet another approach, practiced primarily for the synthesis of mesoporous silicates and aluminosilicates such as MCM-41 and others, involves the use of cooperative templating by assemblies of templates, i.e., liquid crystal templating.<sup>10–12</sup> Capable of such mechanism are surfactant-type templates, i.e., templates that have relatively well separated hydrophobic and hydrophilic ends, where the latter are usually amino groups, phosphates, or sulfates. In the case of the mesoporous materials, the templates have long hydrocarbon chains that form aggregates (micelles), and the resulting frameworks are glassy-like. Here we report the synthesis and structure of a zinc phosphate,  $\text{Zn}_3(\text{PO}_4)_2(\text{PO}_3\text{OH})(\text{H}_2\text{DACH}) \cdot 2\text{H}_2\text{O}$  (referred to as ND-1), with openings made of 24-membered rings, where an assembly of much smaller "surfactant" molecules, 1,2-diaminocyclohexane (DACH), acts as the template.

ND-1 was initially obtained (as a pure solid phase) from a hydrothermal reaction designed to synthesize a templated zinc borophosphate analogous to a known ethylenediamine-templated cobalt borophosphate;<sup>13</sup> therefore, the synthetic mixture contained  $\text{BPO}_4$ , zinc acetate, DACH, and water (molar ratio of



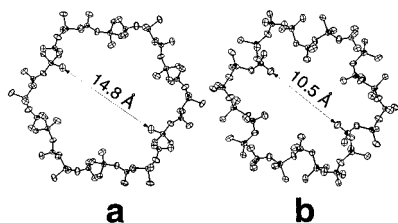
**Figure 1.** General view of the structure of ND-1 projected along the *c*-axis of the hexagonal cell. The framework is built of corner-sharing oxygen tetrahedra centered by zinc (dark gray) and phosphorus (light gray). The channels, made of 24 such tetrahedra, are arranged in a honeycomb array. The templates of *trans*-1,2-diaminocyclohexane and the water molecules (isolated circles) are found near the walls of the channels. The central part of the channels between the templates is hollow (vacuum), with no atoms or molecules found there. The diameter of this tubular empty space is about 8.6 Å (shown).

2:1:2.5:117, 210 °C, 2 days in Teflon-lined autoclaves, pH = 8). Later,  $\text{BPO}_4$  was replaced with  $\text{H}_3\text{PO}_4$ , and it was found that the synthesis can be carried out at lower temperature, 180 °C, and with either zinc acetate or nitrate. The template was deliberately chosen as the 1,2-isomer of diaminocyclohexane rather than the 1,3- or 1,4-substituted isomers because of its well-defined hydrophobic and hydrophilic parts, and therefore the higher potential for liquid-crystal templating. Furthermore, a cyclic template was chosen because of the intrinsic rigidity of the cyclic hydrophobic part and its inability to twist and take different conformations. The only solid product from these reactions was ND-1 in nearly 100 % yield. It crystallizes as very fine, colorless needles, resembling strands of wool or cotton. Fortunately, some of the needles were thick enough for single-crystal X-ray diffraction. A data set was collected from such a crystal, and the structure was successfully refined.<sup>14</sup>

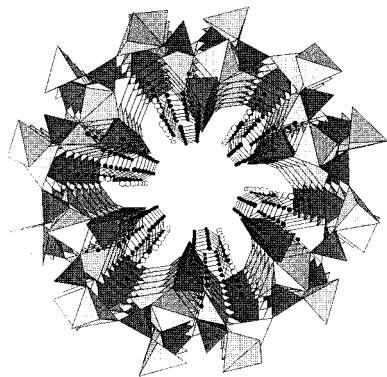
One way of describing the structure of ND-1 is to emphasize its similarity with the mesoporous M41S-class of materials (the better known MCM-41 is one of them), both comprised of close-packed channels in hexagonal, honeycomb arrays (Figure 1). The difference is that the structures of the mesoporous materials cannot be and have not been determined on an atomic level because they lack a long-range order. This, on the other hand, is not the case with ND-1. Here the walls are well defined and are made of corner-sharing tetrahedra of oxygen centered by zinc or phosphorus. All but one of the oxygen atoms are two-bonded, with the exception (O11) being bonded to two Zn and one P atoms, and thus providing a Zn–O–Zn linkage in the structure. The templates in the structure are well defined and without disorder, perhaps due to the extensive hydrogen bonding between the protonated amino groups and oxygen atoms from the framework. Each nitrogen is close to three oxygen atoms: N1 with distances of 2.92(2), 2.91(1), and 2.87(1) Å, and N2 with distances of 2.72(1), 2.86(2), and 2.84(1) Å.

(14) A sixth of a sphere of X-ray diffraction data ( $2\theta_{\text{max}} = 50^\circ$ ) was collected at room temperature on CAD4 with Mo K $\alpha$  radiation from a crystal with dimensions  $0.62 \times 0.04 \times 0.04 \text{ mm}^3$ . Crystal data:  $\text{Zn}_3(\text{PO}_4)_2(\text{PO}_3\text{OH}) \cdot (\text{C}_6\text{H}_{16}\text{N}_2) \cdot 2\text{H}_2\text{O}$ , rhombohedral,  $R\bar{3}$ ,  $Z = 18$ ,  $a = 33.401(7) \text{ \AA}$ ,  $c = 9.241(4) \text{ \AA}$ ,  $V = 8928(5) \text{ \AA}^3$ ,  $R1/wR2 = 5.23/14.71$  for the observed 1793 reflections with  $I \geq 2\sigma_I$ ,  $R1/wR2 = 7.04/15.92$  for all 2272 reflections. The formula of the compound was confirmed by elemental analysis (Analyzed by Galbraith Labs: C, 12.22; H, 3.45; N, 4.88; Zn, 33.25; P, 14.25. Calculated: C, 11.26; H, 3.32; N, 4.42; Zn, 30.93; P, 14.65).

- (1) Corma, A. *Chem. Rev.* **1997**, *97*, 2373.
- (2) Arends, I. W. C. E.; Sheldon, R. A.; Wallau, M.; Schuchardt, U. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1144.
- (3) Ying, J. Y.; Mehnert, C. P.; Wong, M. S. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 56.
- (4) (a) Davis, M. E. *Chem. Eur. J.* **1997**, *3*, 1745. (b) Gier, T. E.; Stucky, G. D. *Nature* **1991**, *349*, 508. (c) Nenoff, T. M.; Harrison, W. T. A.; Gier, T. E.; Stucky, G. D. *J. Am. Chem. Soc.* **1991**, *113*, 378. (d) Harrison, W. T. A.; Gier, T. E.; Moran, K. L.; Nicol, J. M.; Eckert, H.; Stucky, G. D. *Chem. Mater.* **1991**, *3*, 27.
- (5) (a) Férey, G.; Cheetham, A. K. *Science* **1999**, *283*, 1125. (b) Li, H. L.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *Science* **1999**, *283*, 1145.
- (6) Davis, M. E.; Saldarriaga, C.; Montes, C.; Garces, J. M.; Crowder, C. *Nature* **1988**, *331*, 698.
- (7) Estermann, M.; McCusker, L. B.; Baerlocher, C.; Merrouche, A.; Kessler, H. *Nature* **1991**, *352*, 320.
- (8) Hu, Q.; Xu, R.; Li, S.; Ma, Z.; Thomas, J. M.; Jones, R. H.; Chippindale, A. M. *J. Chem. Soc., Chem. Commun.* **1992**, 875.
- (9) Moore, P. B.; Shen, J. *Nature* **1983**, *306*, 356.
- (10) Raimondi, M. E.; Seddon, J. M. *Liq. Cryst.* **1999**, *26*, 305 and references therein.
- (11) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.
- (12) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
- (13) Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2630.



**Figure 2.** ORTEP plots (thermal ellipsoids at the 95% probability level) of the cross sections of the tubular channels of ND-1 at the widest (a) and narrowest (b) places. These alternate along the channels and, when projected, result in the picture shown in Figure 1. Notice that both rings are made of 24 tetrahedra, although the one shown in b is puckered inward.



**Figure 3.** Perspective view of a channel of ND-1, clearly showing its large opening even with the templates and water molecules present.

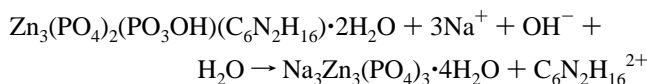
Although a mixture of isomers of 1,2-diaminocyclohexane is used in the synthesis, only the *trans* species act as templates in this compound. Furthermore, the *trans* isomer has two chiral centers, providing two enantiomers, (1*S*,2*S*) and (1*R*,2*R*) species. Since the structure is centrosymmetric, both of those are present. The templates are grouped by threes in triangles with approximately the same *z*-coordinate; i.e., they are at one and the same level along the channel which runs along the *c*-axis of the hexagonal cell. The triangles are stacked along the channels in a staggered fashion and thus appear as hexagons on the two-dimensional projection (Figure 1). Each triangle is composed of species of one and the same chirality, and since the triangles are related by an inversion center, their chirality alternates along the channels. The two water molecules are roughly below and above the templates. Each is hydrogen-bonded to two oxygen atoms from the frame, one with distances of 2.82(1) and 2.76(1) Å, and the other with distances of 2.62(1) and 2.90(1) Å. The two molecules seem to be also hydrogen-bonded to each other with a distance of 2.72(2) Å.

The channels are tubular but not with uniform size: they widen and shrink periodically (Figures 1 and 2). The approximate diameters of the widest and narrowest cross sections of the channels are ca. 14.8 and 10.5 Å, respectively. The tetrahedra pointing toward the center of the channel in Figure 2b are the (PO<sub>3</sub>OH)<sup>2-</sup> groups, and thus the shortest diameter occurs between two hydroxyl groups of a P-centered tetrahedron. In the wider sections, this diameter occurs between oxygen atoms from Zn-centered tetrahedra. The framework density of ND-1 measured by the number of tetrahedra per 1000 Å<sup>3</sup> is not a record low but is definitely one of the lowest, 12.1.

A unique structural feature of ND-1 is that it contains sizable openings, even with the templates present. A diameter of ca. 8.6 Å is measured between the end carbon atoms of two cyclohexanes across the channel (Figures 1 and 3). The existence of such free space or vacuum in a structure as synthesized is unprecedented and very unusual. The structure refinement clearly indicates that there is no electron density in this hollow cylindrical space (the

electron density is less than the maximum of 0.79 e<sup>-</sup>Å<sup>-3</sup> found in the difference Fourier map). This is quite different from other phosphates with extralarge pores, where the openings are stuffed either with water, as in the cacoxenite, or with templates, as in JDF-20 and cloverite. Thus, to “open” the channels in the latter cases, one needs to remove the templates, usually done by calcination. In the case of ND-1, such an operation is unnecessary.<sup>15</sup>

Since the channels of ND-1 (as synthesized) are hydrophobic, our first tests for absorption were carried out with hydrophobic species. Preliminary results based on IR spectroscopy indicate that the compound absorbs species of appropriate size such as benzene, toluene, and cyclohexane, but not the larger *tert*-butylbenzene. Exchange of the diaminocyclohexane dication with other cations was also studied. An unexpected phenomenon was observed in the test with sodium cations in slightly basic solution. Within a few minutes, at room temperature, the needles of ND-1 began to disappear, and at the same time crystals with cubic shape grew on the bottom of the beaker. After about 2 h, the process was complete, and the new crystals were removed, washed, and examined by X-ray diffraction. It was found that they are also of a material with open-framework structure, Na<sub>3</sub>Zn<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>·4H<sub>2</sub>O, that is isostructural with sodalite, Na<sub>3</sub>Al<sub>3</sub>Si<sub>3</sub>O<sub>12</sub>·4H<sub>2</sub>O. Thus, the following equation can be written:



The synthesis of Na<sub>3</sub>Zn<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>·4H<sub>2</sub>O from zinc oxide, phosphoric acid, and sodium hydroxide at room temperature has been studied before.<sup>4c</sup> Apparently, in our case, ND-1 disassembles at these conditions, and a more rigid structure with smaller openings assembles at the same time. Therefore, this soft-chemistry process can be classified as a process of self-assembly of sodalite from an advanced precursor, ND-1, and sodium cations at very mild conditions. This seems to be the first case of zeolitic interconversion at such a low temperature and in such record times. Preliminary results also suggest that, in the presence of other cations (K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>, (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup>, and (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N<sup>+</sup>), ND-1 transforms into other, unknown products, some of which are in the process of being structurally characterized.

Finally, we should point out the potential of ND-1 to be used as a tool for separation and recognition of the *cis* and *trans* isomers of 1,2-diaminocyclohexane. A mixture of the two can be heated in an autoclave with appropriate amounts of a zinc salt and phosphoric acid (both relatively inexpensive). This will result in a relatively pure *cis* isomer in the liquid and pure *trans* isomer in the solid. Furthermore, the latter will be composed of the two enantiomers in *exactly* 1:1 ratio. Next, the solid is placed in a Na<sup>+</sup>-containing basic solution, where solid sodalite is formed and the two enantiomers are released in the solution. Work is in progress on possible recovery of plain zinc phosphate from the sodalite and its repeated use for synthesis of ND-1.

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**Supporting Information Available:** An X-ray crystallographic file, in CIF format, is available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) Upon heating, ND-1 is stable up to 200 °C (kept for 5 h at that temperature). It loses the template and its structure collapses at temperatures above 350 °C. It produces Zn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> above 700 °C.