CHEMISTRY OF
MATERIALS

VOLUME 6, NUMBER 4 APRIL 1994

Communications

The First Octahedral–Trigonal Bipyramidal–Tetrahedral Framework Oxide: Hydrothermal Synthesis and Structure of $K[Ni(H_2O)_2Al_2(PO_4)_3]$

Linda M. Meyer and Robert C. Haushalter*

NEC Research Institute, 4 Independence Way
Princeton, New Jersey 08540

Received November 23, 1993
Revised Manuscript Received February 1, 1994

Synthetic tetrahedral framework aluminophosphates (AlPOs) and metal aluminum phosphates (MeAlPOs), many of which were first synthesized by Flanigen, Wilson, and co-workers,[1] comprise a large and important class of structurally diverse microporous materials. Most of the known aluminophosphates have neutral frameworks and Al/P ratios of one and do not contain Al–O–Al or P–O–P bonds. Although many have tetrahedral frameworks, there are also examples of AlPOs in which the aluminum is either 5 or 6 coordinate. Aluminum can be found in an octahedral environment in $AlPO_4$-15[2] and the recently prepared fluoroaluminum phosphate $AlF(HPO_4)\cdot en$.[3] $AlPO_4$-21 contains both tetrahedral and trigonal bipyramidal aluminum.[4] Metal aluminophosphates have been synthesized with a variety of metals substituted mainly into tetrahedral aluminum sites.[5] Recently, microporous solids have been extended into stoichiometric octahedral–tetrahedral framework materials with the discovery of certain molybdenum phosphates[6] as well as the ETS[7] and other titanium silicate materials.[8] Although unexamined for microporous behavior, several open-framework, organically templated vanadium phosphates have been discovered.[9] Here we describe the hydrothermal synthesis of $K[Ni(H_2O)_2Al_2(PO_4)_3]$ (1), a novel potassium nickel aluminophosphate containing octahedral nickel, trigonal-bipyramidal aluminum, and tetrahedral phosphorus in the anionic oxide framework. To the best of our knowledge, the title compound represents the first example of a framework oxide built up from these three types of polyhedron.

The hydrothermal reaction of $NiCl_2\cdot 6H_2O$, $AlCl_3\cdot 6H_2O$, KCl, $(CH_3)_4NOH$, H_3PO_4, and H_2O in molar ratio of 3:0.20:6:6:10:400 at 150 °C for 100 h yields yellow crystals of 1 in 81% yield based on Al. The product is the only solid precipitating from solution and is single phase based on comparison of its powder X-ray diffraction pattern to the pattern simulated from the atomic coordinates obtained from the single-crystal X-ray structure.[10] Although the cation from the tetramethylammonium hydroxide was not incorporated into the framework, it was necessary for the synthesis of the product. Decreasing the Ni:Al ratio below 15:1 resulted in the appearance of an aluminophosphate phase in the product. The excess Ni^{2+} remains in solution in the green supernatant.

The aluminophosphate $K[Ni(H_2O)_2Al_2(PO_4)_3]$ crystallizes in the monoclinic space group $C2/c$, and a polyhedral representation of the unit cell contents projected down

---

(1) Wilson, S. T.; Flanigen, E. M.; In *Zeolite Synthesis*; Occelli, M. L., Robson, H. E., Eds.; American Chemical Society: Washington, DC, 1989; p 329.

(2) Szostak, R. *Molecular Sieves Principles of Synthesis and Identification*; Van Nostrand Reinhold: New York, 1989; Chapter 4, ref 120.

(3) Riou, D.; Koiseau, Th. *J. Solid State Chem.* **1993**, *102*, 4.

(4) Bennett, J. M.; Cohen, J. M.; Artiolo, G.; Pluth, G.; Smith, J. V. *Inorg. Chem.* **1985**, *24*, 188.

(5) Flanigen, E. M.; Wilson, S. T. U.S. Patent 4,567,029, 1986.

(6) Haushalter, R. C.; Mundi, L. A. *Chem. Mater.* **1992**, *4*, 31.

(7) Kuznicki, S. M. U.S. Patent 4,853,202. Kuznicki, S. M.; Thrush, A. K. Eur. Patent 0405978A1.

(8) Chapman, D. M.; Roe, A. L. *Zeolites* **1990**, *10*, 730.

(9) Haushalter, R. C.; Soghomonian, V.; Zubieta, J.; O'Connor, C. J.; Chen, Q. *Science* **1993**, *259*, 1596. Haushalter, R. C.; Soghomonian, V.; Zubieta, J.; Chen, Q. *Angew. Chem.* **1993**, *32*, 4, 610. Haushalter, R. C.; Soghomonian, V.; Zubieta, J.; Chen, Q. *Chem. Mater.*, in press.

(10) Crystal data for $K[Ni(H_2O)_2Al_2(PO_4)_3]$ (1): monoclinic, space group $C2/c$ (No. 15); $a = 13.075(1)$ Å, $b = 10.114(1)$ Å, $c = 8.720(1)$ Å, $\beta = 108.158(10)°$, $V = 1095.7(3)$ Å^3, $Z = 4$, $D_{calc} = 2.865$ g/cm^3, μ(Mo Kα) = 28.35 cm^{-1}, $\lambda = 0.7107$ Å, $R = 0.025$, $R_w = 0.029$. Data were collected on a yellow chunk crystal of dimensions 0.1 mm × 0.1 mm × 0.2 mm using a Rigaku AFC7R four-circle diffractometer at 20 °C. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were found in the final difference Fourier map.

0897-4756/94/2806-0349$04.50/0

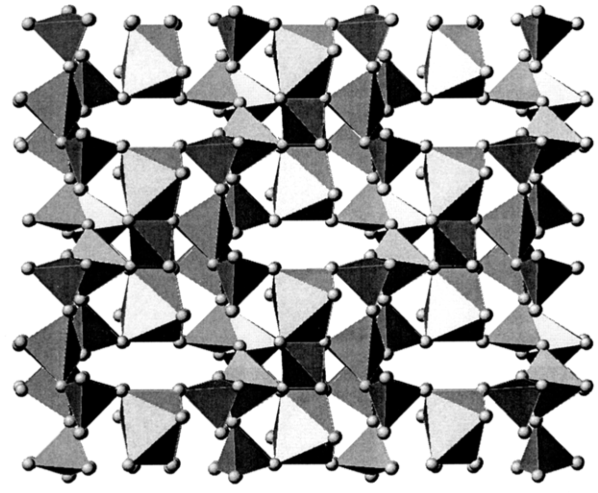

Figure 1. Polyhedral representation of 1 projected down [001]. The potassium cation has been omitted for clarity.

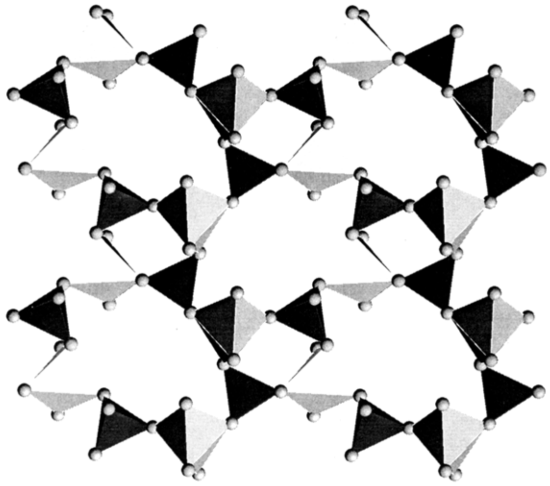

Figure 2. View perpendicular to aluminum phosphate layer.

[001] is shown in Figure 1. The anionic framework is built up from NiO_6 octahedra, AlO_5 trigonal bipyramids and PO_4 tetrahedra in the ratio of 1:2:3. The three-dimensional structure can be conceptualized as planar aluminophosphate "layers", that lie in planes perpendicular to a at $a = {}^1/_4$ and ${}^3/_4$ (Figure 1), bridged together by P^{5+} and $Ni(H_2O)_2{}^{2+}$ moieties that lie in planes perpendicular to a at $a = 0$ and ${}^1/_2$. One of these aluminophosphate layers, formed from the condensation of eight rings of alternating AlO_5 trigonal bipyramids and PO_4 tetrahedra, is shown in Figure 2. Both the aluminum- and phosphorus-centered polyhedra in the layer provide three vertices for the interlayer bonding to neighboring polyhedra. In addition, each phosphate tetrahedron has a P–O bond that extends above and below the plane of the AlPO layer and is bonded to the nickel. The AlO_5 trigonal bipyramid forms two bonds outside the AlPO layer, through both an equatorial and axial bond of the bipyramid, one to nickel and one to the interlayer P^{5+}. The Ni^{2+} cations bridging the aluminophosphate layers together have a very unusual coordination environment (Figure 3). Two trans vertices of the NiO_6 octahedron are occupied by terminal aquo ligands (Ni–O2 = 2.091(2) Å) and two by cis O atoms bridged to two crystallographically equivalent phosphate tetrahedra (Ni–O1 = 1.998(2) Å). The remaining two vertices (Ni–O3 = 2.146(2) Å) are three-coordinate oxygens that are bonded to two AlO_5 bipyramids and also form a shared edge with an adjacent PO_4 tetrahedron. The AlO_5 polyhedron displays angles of 116.96(10)°–123.76(9)° for the O–Al–O equatorial interactions and 175.94(9)° for the axial O6–Al–O3 angle. The axial Al–O bonds (1.882(2)–1.927(2) Å) are slightly longer than the equatorial Al–O bonds of 1.771(2)–1.797(2) Å. The potassium cation is eight coordinate with bond distances ranging from 2.821(2)–3.301(2) Å.

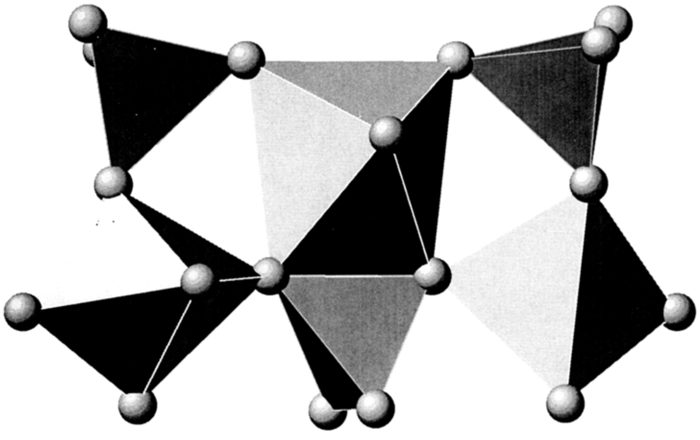

Figure 3. Coordination environment around the octahedral Ni showing the connectivity to the aluminum and phosphorus via a three-coordinate oxygen. The nickel and phosphorus polyhedra share edges.

A new type of polyhedral connectivity has been observed in the easily synthesized octahedral–trigonal bipyramidal–tetrahedral framework found in the mixed-metal phosphate $K[Ni(H_2O)_2Al_2(PO_4)_3]$. These results expand the known modes of connectivity available to polyhedral oxide framework materials and suggest that other transition and main-group metals may be incorporated into oxides via hydrothermal syntheses. For example, we will shortly report on other Ni, V, and Mn phosphates prepared by this method.

Supplementary Material Available: Summary of the crystallographic data and tables of atomic coordinates with B(eq), U_{ij}, bond lengths and angles, and nonbonded contacts (16 pages); table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.