# Aluminoborate-Based Molecular Sieves with 18-Octahedral-Atom Tunnels**

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Microporous frameworks composed of tetrahedra, particularly zeolites, have been extensively studied. These materials are of technological importance as shape-selective catalysts and ion-exchange materials and are widely used in various industrial and technological processes.[1] On the other hand, although a number of microporous materials consisting of mixed octahedra/tetrahedra were established in recent years,[2] microporous frameworks based purely on octahedra are rare. The todorokite family of manganese oxides,[3] including pyrolusite, todorokite, hollandite, and romanechite, is a well-known example among the pure-octahedron frameworks. In these materials, the octahedra share edges to form cubic close-packed rock salt (111) layers, which are interconnected by sharing corners at 90° angles (rutile-like connection), forming one-dimensional tunnels with different pore sizes. The large square tunnels and mixed manganese valences endow these materials with potential applications as redox catalysts, batteries, and chemical sensors.[4] Here we report the novel aluminoborate PKU-1, in which $AlO_6$ octahedra share edges to form a three-dimensional porous framework consisting of 18- and 10-ring windows. The search for new zeolite-like aluminoborates was carried out several years ago, and several aluminoborates and aluminum boron oxide chlorides were identified under hydrothermal conditions, but their stuctures remain unknown.[5]

Aluminoborate PKU-1 was synthesized by reaction of $AlCl_3 \cdot 6H_2O$ with an excess of $H_3BO_3$ at 240 °C in an autoclave (yield: 95 % in Al), whereby the boric acid was used as both reaction medium and reactant. The product consists of needle-shaped polycrystallites. X-ray diffraction identified a trigonal structure ($R\bar{3}$) with lattice parameters $a = 22.0381(2)$ and $c = 7.0261(1)$ Å at room temperature. Analysis of boron and aluminum by inductively coupled plasma emission spectroscopy (ICP-ES) gave a B/Al ratio of about 2. The $^{27}$Al MAS-NMR, $^{11}$B MAS-NMR, and IR data indicated that the Al and B atoms are exclusively in octahedral and triangular coordination, respectively. The detailed structure of PKU-1 was established by analysis of the XRD data with an ab initio method and subsequently by Rietveld refinements with the GSAS program,[6,7] which allowed all non-hydrogen atoms in the compound to be located.[8] The refined structural parameters are listed in the Supporting Information. The presence of protons in the structure was established by consideration of charge balance, as well as thermogravimetric analysis (TGA), IR spectroscopy, and valence calculation.

Figure 1 shows the structure of PKU-1 projected along the *c* axis. The structure can be considered as a framework of octahedra that is enveloped by triangular borate groups. The aluminum atoms are all octahedrally coordinated, and the octahedra share edges to form a framework with three-dimensional porosity. The structure contains two crystallographically independent types of Al atoms [Al1-(18*f*) and Al2-(9*d*)]. The Al1 octahedra share three edges with two Al1 and one Al2 octahedra and act as "nodes" in the framework. The Al2 atoms, on the other hand, share two opposite edges with Al1 octahedra, leaving two opposite corners as terminal oxygen atoms. An alternative description of the framework is that the Al1 octahedra form one-dimensional edge-sharing chains along the *c* axis (threefold helix with an approximate Al1-Al1-Al1 angle of 120°). The Al2 octahedra share two opposite edges with the Al1 chains to form a three-dimensional porous framework. Thus Al2 octahedra act as "girders" in the framework. Figure 2 displays a perspective view of the

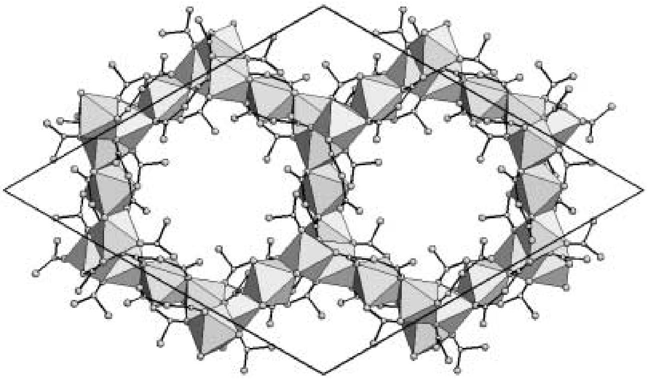

***Figure 1.*** Projection of the PKU-1 structure along the *c* axis; $AlO_6$ octahedra are shown as polyhedra, and oxygen and boron atoms as dark and light spheres, respectively; water molecules in the channels are omitted for clarity.

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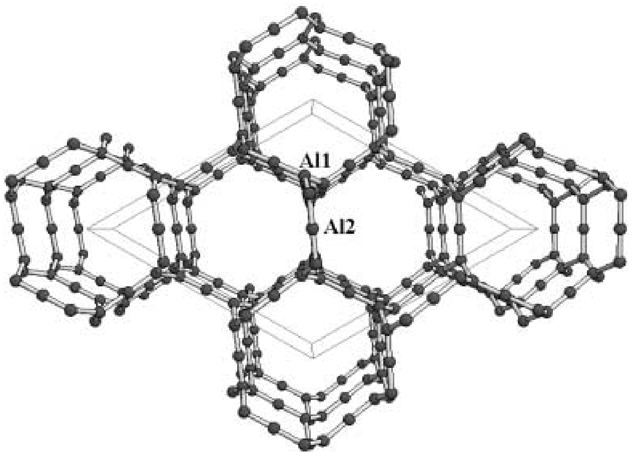

*Figure 2.* Perspective view of the framework of octahedra in PKU-1 showing the large, parallel hexagonal channels (18-ring) along [001] and the smaller rectangular channels (10-ring) along {100}.

framework of PKU-1, which clearly shows the connectivity of octahedra in the structure. The cavity of the framework is three-dimensional and contains 18-ring hexagonal channels along the [001] direction and 10-ring rectangular channels along each of the {100} directions. The structural model of PKU-1 was also supported by high-resolution TEM data (Figure 3). The HREM image (central inset), simulated by using the structural parameters of PKU-1, agrees reasonably well with the observed pattern. In addition, electron diffraction (insert left) also confirms the trigonal cell of the structure.

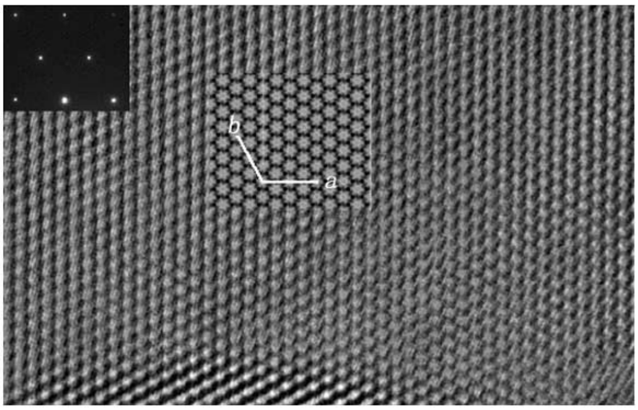

*Figure 3.* HREM image of PKU-1 in the basal plane; the electron diffraction pattern (top, left inset) shows a typical trigonal symmetry. The inset at the center is a simulated HREM image based on the structural parameters of PKU-1. The basal axes *a* and *b* are shown in the figure, and the length of the axis bars is about 44 Å.

The framework of edge-sharing Al octahedra in PKU-1 is highly negatively charged ($[Al_3O_{10}]^{11-}$). This is a common feature of three-dimensional porous frameworks of octahedra and may also be the reason that these frameworks are rare. To stabilize the octahedral framework, other positively charged species are needed. As shown in Figure 1, all of the oxygen atoms of the octahedral framework are further shared by surrounding borate groups [i.e., $BO_2(OH)$ and $B_2O_4(OH)$] that compensate most of the negative charges ($[Al_3B_6O_{12}(OH)_4]^-$). The remaining negative charge could be compensated by countercations in the channels. In this case, it is likely that protons act as the countercations. The IR spectrum of a sample after calcination at 200 °C under vacuum clearly shows three distinct OH vibrations at 3180, 3440, and 3650 $cm^{-1}$ for the hydroxy groups (see Supporting Information). The overall composition of PKU-1 can be expressed as $HAl_3B_6O_{12}(OH)_4$.

The borate groups partially block the channels of the framework and thus reduce the porosity of the structure. Figure 4 shows the structures of the 18- and 10-rings. The $B_2O_4(OH)$ groups are located within the 10-ring rectangular windows and almost completely block the channels along the {100} directions. The $BO_2(OH)$ groups are located within the 18-ring windows and narrow the channels along the [001] direction. The O–O distances of about 5.8 Å between the terminal oxygen atoms on borate groups and about 9.5 Å between those on the Al octahedra correspond to columns 6.7 Å and 11.0 Å in diameter, respectively. The nitrogen adsorption isotherm of a PKU-1 sample degassed at 200 °C under vacuum was characteristic of a microporous material, with a maximum uptake of about 71.4 $cm^3$ of nitrogen per gram of sample.

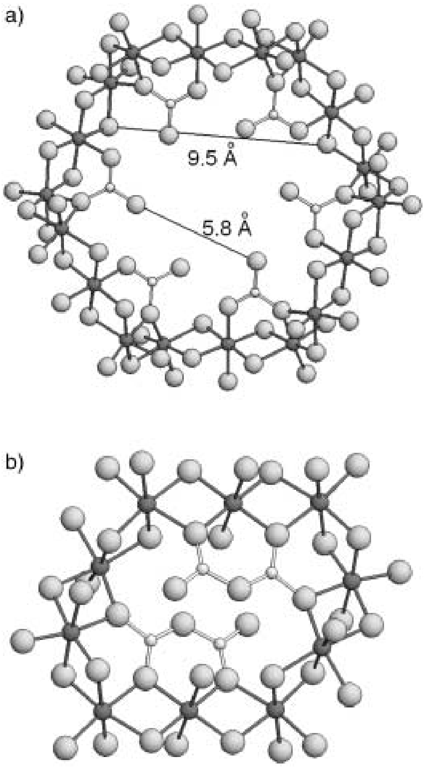

*Figure 4.* a) 18- and b) 10-ring windows in PKU-1; the borate groups in the channel are also shown. The distances of 5.8 and 9.5 Å shown in the 18-ring are between crystallographically equivalent terminal oxygen atoms and oxygen atoms of the octahedra, which result in diameters of 6.7 and 11.0 Å, respectively, for the channel.

*Table 1:* Reaction and lattice parameters for PKU-1.[a]

| Compound | Synthesis conditions | | | | Lattice parameter | |
|---|---|---|---|---|---|---|
| | Reactants | | *T* [°C] | *t* [d] | *a* [Å] | *c* [Å] |
| $HAl_3B_6O_{12}(OH)_4$ | 5 mmol $AlCl_3 \cdot 6H_2O$ | 100 mmol $H_3BO_3$ | 240 | 4 | 22.0381(2) | 7.0261(1) |
| $HGa_3B_6O_{12}(OH)_4$ | 5 mmol $Ga_2O_3$ | 200 mmol $H_3BO_3$ | 220 | 10 | 22.6212(9) | 7.2441(8) |
| $HAl_{2.4}Fe_{0.6}B_6O_{12}(OH)_4$ | 4 mmol $AlCl_3 \cdot 6H_2O$<br>1 mmol $Fe(NO_3)_3 \cdot 6H_2O$ | 100 mmol $H_3BO_3$ | 220 | 14 | 22.2130(5) | 7.1024(3) |
| $HAl_{2.5}Cr_{0.5}B_6O_{12}(OH)_4$ | 4 mmol $AlCl_3 \cdot 6H_2O$<br>1 mmol $Cr(NO_3)_3 \cdot 6H_2O$ | 100 mmol $H_3BO_3$ | 220 | 14 | 22.2041(9) | 7.0716(1) |

[a] The lattice constants were determined by refinement with EXTRA.

The structure refinement also indicated that the as-synthesized sample contains a considerable number of partially ordered water molecules in the 18-octahedron channels. These water molecules are mobile and can be removed completely without affecting the integrity of the framework structure. Structure refinement carried out on a PKU-1 sample calcined at 200 °C showed that the residual electron density in the channels was completely removed (see Supporting Information). Furthermore, TGA shows two-stage weight loss. The weight loss below 200 °C (ca. 8.1 wt %) originates from removal of water, and that between 300 and 600 °C (ca. 10.1 wt %) is related to dehydration of the borate hydroxy groups. Above 600 °C the framework eventually collapses.

The microporous materials known so far are mostly based on corner-sharing tetrahedra, and octahedron-based molecular sieves are rare. One reason for this might be the high negative charge of the three-dimensional porous frameworks of octahedra for common $M^{III}$ and $M^{IV}$ cations. Two different approaches may reduce the negative charge: sharing the octahedral edges more extensively throughout the framework or compensating with other positively charged species. The OMS (octahedral molecular sieves) family of manganese oxides[4] exemplifies extensive sharing of octahedral edges, in this case to form rock salt (111) layers. The oxygen atoms in this family all exhibit threefold coordination by $Mn^{4+}$ and $Mn^{2+}$. PKU-1 is a representative in which the negative charge is compensated by borate groups. In the structure of PKU-1, most of the oxygen atoms on the framework of octahedra of PKU-1 are also threefold coordinated by Al and B (except for the opposite vertices on the Al2-octahedron, which are two-coordinate). Such a mode of compensation allows the formation of a three-dimensional framework of octahedra containing tunnels.

It is noteworthy that this octahedron-based molecular sieve was synthesized in boric acid flux without using any organic template. Although the reaction mechanism is not yet understood, the formation of the microporous structure implies the assembly of borate groups and water molecules, perhaps mediated by hydrogen bonding during the reaction. In fact, in addition to PKU-1, many new polyborates, including rare-earth polyborates and transition-metal polyborates, were obtained.[9] Moreover, some other metal ions can also be accommodated at the octahedral sites in the PKU-1 structure. Galloborate ($HGa_3B_6O_{12}(OH)_4$) also crystallizes in the PKU-1 structure under the same reaction conditions. The lattice constants are significantly larger than than those of the aluminum analogue, as shown in Table 1. We also applied similar reaction conditions to the transition metal salts and found that most transition metals do not themselves form PKU-1 structures, but can partially replace Al to form solid solutions such as $HAl_{2.4}Fe_{0.6}B_6O_{12}(OH)_4$ and $HAl_{2.5}Cr_{0.5}B_6O_{12}(OH)_4$. As shown in Table 1, substitution by transition-metal ions modifies the lattice parameters and the porosity of the frameworks. In terms of potential applications, the octahedral molecular sieves containing d-block elements are considerably more interesting because they may provide a means of tailoring not only chemical and physical properties such as catalysis, ion exchange, and molecular sieving, but also electronic properties.

## *Experimental Section*

PKU-1 was synthesized by direct reaction of aluminum salts with boric acid in a flux of boric acid in a closed autoclave. In a typical reaction $AlCl_3 \cdot 6H_2O$ (5 mmol) and $H_3BO_3$ (100 mmol) were charged to a 50 cm³ Teflon autoclave, and the mixture was heated at 240 °C for four days. After cooling to room temperature, the solid (containing PKU-1 and residual $H_3BO_3$) was washed with hot water (50 °C) until the residual boric acid was completely removed. The yield was about 95 % in Al. Other aluminum sources, such as $Al_2O_3$ and $Al(NO_3)_3$, also yielded the same product. Ga-PKU-1 and transition-metal-substituted PKU-1 (AlCr-PKU-1 and AlFe-PKU-1) were synthesized from gallium oxide and the transition-metal nitrates by a similar method at 220 °C for 10–14 days. Table 1 summarizes the reaction conditions for these compounds. The degree of substitution by transition-metal cations was analyzed by the ICP method.

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[8] Powder XRD data of PKU-1 were collected at room temperature on a Bruker D8 diffractometer in the Bragg–Brentano geometry with a curved germanium primary monochromator ($Cu_{K\alpha1}$, $\lambda =$ 1.5406 Å). Tube voltage and current were 50 kV and 40 mA. Step-scan size and time: 0.02° ($2\theta$) and 30 s. The patterns were indexed to trigonal unit cells, $a = 22.0392(2)$ and $c = 7.02643(8)$ Å by using TREOR90-PowderX,[6] and the analysis of the observed systematic absences narrowed the possible space groups to $R\bar{3}$, $R3$, $R32$, $R3m$, and $R\bar{3}m$. PKU-1 does not show nonlinear optical behavior, so the space group was restricted to $R\bar{3}$ or $R\bar{3}m$. The crystal structure was established by using EXPO with space group $R\bar{3}$ and was further developed by difference Fourier analysis during the Rietveld refinement.[6,7] All non-hydrogen atoms in the structure were refined with geometric constraints of triangular borate groups. The first reflection peak at about 8.0° was not used in the structure refinement. The number of contributing reflections was 421 with 29 structure and profile variables in the final refinement. The residual factors of the refinement were $R_{wp} = 0.069$ and $R_p = 0.049$. The Rietveld refinement was also carried out for a PKU-1 sample calcined at 200 °C. The structure parameters are almost the same as those of the as-synthesized sample (with $R_{wp} = 0.048$ and $R_p = 0.036$), but the disappearance of all of the electron density in the channels indicated complete removal of the mobile water from the channels. Crystallographic data, atomic parameters, and selected bond lengths and angles are given in the Supporting Information. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-413233.

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