Inorg. Chem. **2007**, *46*, 4772–4774

Inorganic Chemistry
Communication

Square-Pyramidal/Triangular Framework Oxide: Synthesis and Structure of PKU-6

Tao Yang,[†] Jing Ju,[†] Guobao Li,[†] Fuhui Liao,[†] Xiaodong Zou,[‡] Feng Deng,[§] Lei Chen,[§] Yingxia Wang,[†] and Jianhua Lin*,[†]

Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China, Structural Chemistry, Stockholm University, SE-10691 Stockholm, Sweden, and State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematic, Chinese Academy of Sciences, Wuhan 430071, China

Received January 16, 2007

PKU-6, a new aluminoborate ($HAl_2B_3O_8$), has been synthesized in a closed system at 400 °C. The structure of PKU-6, characterized by using powder and single-crystal X-ray diffraction, consists of AlO_5 square-pyramidal chains and B_3O_7 groups, which are interconnected and form a three-dimensional framework. The ^{27}Al NMR study indicates that the isotropic chemical shift of pyramidal Al is 34.6 ppm with a large quadrupolar coupling constant ($C_Q = 4.2$ MHz), mainly due to a nonspherical coordination environment.

Al is an essential component in many microporous compounds. Generally, Al atoms adopt 4- or 6-fold coordination. In zeolites, for example, Al atoms are 4-coordinated in tetrahedral geometry. The 6-coordination Al is common in condensed and microporous oxides; in $AlPO_4$-15,[1] for example, Al octahedra and P tetrahedra share corners, forming a porous structure. Purely octahedral frameworks were also found in aluminoborates, PKU-1[2] and PKU-5,[3] in which the Al octahedra share edges, forming extended porous frameworks. In contrast, 5-coordinated Al is rare in extended ionic arrays. In addition, the 5-coordinated Al atoms identified in amorphous aluminates[4] and microporous compounds[5] have mostly trigonal-bipyramidal geometries, and distorted square-pyramidal geometry is rare.[6] Here we report a new hydrated aluminoborate $HAl_2B_3O_8$ (PKU-6), in which the Al ions are 5-coordinated in regular square-pyramidal geometry.

PKU-6 was synthesized by the direct reaction of $AlCl_3$ with excess B_2O_3/H_3BO_3 in a closed system at 400 °C for 1 week.[7] The reaction temperature is crucial for the formation of PKU-6. At lower temperatures, other aluminoborates, such as PKU-1[2] or PKU-5,[3] appear. The obtained crystals of PKU-6 were, in general, small (see the Supporting Information); thus, the structure was first established by an ab initio method with powder X-ray diffraction data,[8] which was then further confirmed and refined by single-crystal X-ray diffraction techniques on a small crystal (30 μm × 30 μm × 100 μm).[11]

PKU-6 contains nine crystallographically independent atoms: one Al, five O, two B, and one H. Figure 1 shows a fragment of the structure, where one can see that the Al atom is 5-coordinated in square-pyramidal geometry, while the B atoms are triangularly coordinated. Noted that O1, O2, B1, and H1 reside on a mirror plane, that is, the fragments are connected along the *b* axis, forming a one-dimensional AlO_5 chain and B_3O_7 groups (Figure 2a). Table 2 lists the selected bond distances and angles. The bond distances and

---

* To whom correspondence should be addressed. E-mail: jhlin@pku.edu.cn.

[†] Peking University.

[‡] Stockholm University.

[§] Chinese Academy of Sciences.

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

(2) Ju, J.; Lin, J.; Li, G.; Yang, T.; Li, H.; Liao, F.; Loong, C. K.; You, L. *Angew. Chem., Int. Ed.* **2003**, *42*, 5607−5610.

(3) Ju, J.; Yang, T.; Li, G.; Liao, F.; Wang, Y.; You, L.; Lin, J. *Chem.*−*Eur. J.* **2004**, *10*, 3901−3906.

(4) Wilcox, L.; Burnside, G.; Kiranga, B.; Shekhawat, R.; Mazumder, M. K.; Hawk, R. M.; Lindquist, D. A.; Burton, S. D. *Chem. Mater.* **2003**, *15*, 51−56.

(5) (a) Bennett, J. M.; Cohen, J. M.; Artioli, G.; Pluth, J. J.; Smith, J. V. *Inorg. Chem.* **1985**, *24*, 188−193. (b) Meyer, L. M.; Haushalter, R. C. *Chem. Mater.* **1994**, *6*, 349−350. (c) Tuel, A.; Jorda, J. L.; Gramlich, V.; Baerlocher, C. *J. Solid State Chem.* **2005**, *178*, 782−791. (d) Kongshaug, K. O.; Fjellvåg, H.; Lillerud, K. P. *Microporous Mesoporous Mater.* **1999**, *32*, 17−28.

(6) (a) Wang, K.; Yu, J.; Miao, P.; Song, Y.; Li, J.; Shi, Z.; Xu, R. *J. Mater. Chem.* **2001**, *11*, 1898−1902. (b) Yuan, H. M.; Chen, J. S.; Shi, Z.; Chen, W.; Wang, Y.; Zhang, P.; Yu, J. H.; Xu, R. R. *J. Chem. Soc., Dalton Trans.* **2000**, 1981−1984. (c) Kongshaug, K. O.; Fjellvåg, H.; Lillerud, K. P. *J. Mater. Chem.* **1999**, *9*, 1591−1598.

(7) A typical preparation of PKU-6 was to charge a mixture of $AlCl_3$ (1.10 g), B_2O_3 (4.50 g), and H_3BO_3 (2.55 g) to a 25 mL platinum autoclave. After the system was heated at 400 °C for 1 week, a single-phase product could be isolated by removing excess boric acid and boron oxide with hot water (80 °C). The chemical formula established by structure determination is $Al_2(OH)B_3O_7$, which is further confirmed by chemical analysis (ICP; B:Al = 1.57) and TGA analysis (weight loss at 700 °C, obsd 3.95 wt %, calcd 4.0 wt %).

10.1021/ic070073k CCC: $37.00

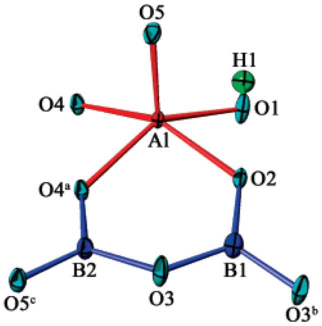

Figure 1. Fragment in the structure of PKU-6. Symmetry transformations used to generate equivalent atoms: a, $-x$, $-y$, $-z$; b, x, $-y + {}^1/_2$, z; c, $-x + {}^1/_2$, $-y$, $z + {}^1/_2$.

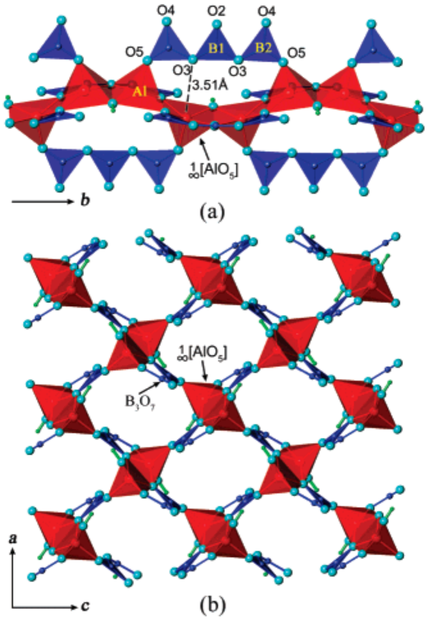

Figure 2. (a) One-dimensional AlO_5 square-pyramidal chain and the linkage to the B_3O_7 borate groups in PKU-6 (AlO_5, red polyhedra; BO_3, dark-blue triangles; O, cyan; H, green balls). (b) Projection of the PKU-6 structure along the *b* axis.

Table 1. Crystallographic Data of PKU-6 Obtained from a Single-Crystal X-ray Diffraction Study

formula	$HAl_2B_3O_8$
fw	215.40
cryst size (mm)	0.03 × 0.03 × 0.1
color	colorless
space group	*Pnma*
a (Å)	7.4832(15)
b (Å)	10.528(2)
c (Å)	8.8525(18)
V (Å^3)	697.4(2)
Z	4
ρ_{calcd} (g/cm^3)	2.052
μ(Mo Kα) (mm^{-1})	0.424
indep reflns	682
$I > 2\sigma(I)$	616
θ range (deg)	3.01−25.48
R1 [$I > 2\sigma(I)$]^a	0.0311
wR2 (all data)^a	0.1373

angles are regular. As shown in Figure 2a, the AlO_5 square pyramids share opposite basal edges in the chain; thus, it can also be considered an edge-sharing AlO_6 octahedral chain, but the axial corners are removed alternatively on each side for a pair of AlO_6 octahedra.

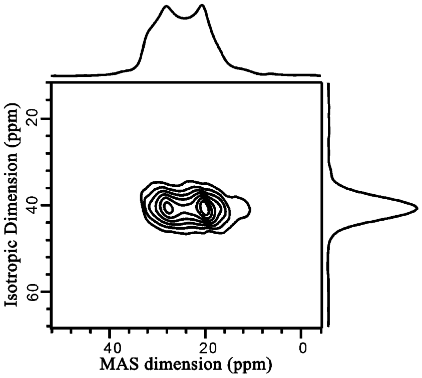

Figure 3. ^{27}Al 3Q MAS NMR spectrum of PKU-6. The obtained isotropic chemical shift is 34.6 ppm with a quadrupolar coupling constant $C_Q = 4.2$ MHz and an asymmetry parameter $\eta = 0.38$.

The AlO_5 square-pyramidal chains are interconnected by B_3O_7 groups, forming a three-dimensional framework structure (Figure 2b). The five terminal O atoms (O2, O4, O4, O5, and O5) on the B_3O_7 group are shared with AlO_5 chains, among which O2 and the two O4 atoms are chelately coordinated to Al, forming three-membered rings (Al + 2B), and the two O5 atoms are bonded axially to the Al pyramids of the neighboring chain. It is known that the Al + 2B three-ring unit is a fundamental building unit in octahedra containing frameworks and, additionally, is crucial to stabilizing porous aluminoborate frameworks.[3] Interestingly, the two bridged O atoms (both O3) on B_3O_7 are located just above the basal square planes of the AlO_5 pyramids, as if to complete the octahedral coordination for Al ions. However, these Al−O3 distances (about 3.51 Å) are too long to be an actual Al−O bond. Consequently, such structural arrangement prevents any further coordination to Al, so that the coordination geometry of Al in PKU-6 is a square pyramid instead of an octahedron.

PKU-6 contains a single square-pyramidal Al site, so it is a suitable model compound to study the local symmetry

---

(8) Powder X-ray diffraction data was collected at room temperature on a Bruker D8 diffractometer with a curved Ge primary monochromator (Cu Kα_1; $\lambda = 1.5406$ Å). The tube voltage and current were 40 kV and 40 mA, respectively. Transmission mode was used, and the sample was monitored on a planar plastic film. The diffraction pattern was recorded with a PSD detector with step scan size/time of 0.0144° (2θ)/40 s. The powder pattern was indexed with *PowderX*,[9] which yielded an orthorhombic cell: $a = 7.4723(3)$ Å, $b = 10.5285(5)$ Å, and $c = 8.8625(5)$ Å. The systematic absences narrowed the possible space groups to *Pnma* and *Pna*2$_1$. The structure model was therefore established in *Pnma* by using a model annealing technique with *TOPAS*.[10] All of the non-H atoms were located, and the structure was refined with the Rietveld method. A six-term Chebyshev polynomial and a $1/2\theta$ term were used to model the background. The peak shapes were modeled with the pseudo-Voigt function. Soft restraints were applied to the thermal displacement parameters of the atoms. The final refinement converged to $R_p = 0.033$, $R_{wp} = 0.048$, and GOF = 3.61.

(9) Dong, C. *J. Appl. Crystallogr.* **1999**, *32*, 838.

(10) *TOPAS V2.1: General Profile and Structure Analysis Software for Powder Diffraction Data*; Bruker AXS: Karlsruhe, Germany.

(11) Single-crystal diffraction data were collected on a small single crystal of PKU-6 (30 μm × 30 μm × 100 μm) at 293 K on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) by using the $\omega - 2\theta$ scan method. According to the systematic extinctions, the space groups *Pnma* and *Pna*2$_1$ were derived. The centrosymmetric group was found to be correct during the structure refinement, while the noncentrosymmetric solution led to negative anisotropic displacement parameters. The structure was refined on F^2 with full-matrix least-squares methods using *SHELXS-97* and *SHELXL-97*[12] programs.

Table 2. Selected Bond Distances (Å) and Angles (deg) for PKU-6

Al−O5	1.7447(17)	O5−Al−O1	108.33(11)	O2−B1−O3	121.43(15)
Al−O1	1.8025(15)	O5−Al−O2	101.88(10)	O2−B1−O3	121.43(15)
Al−O4^a	1.8359(17)	O5−Al−O4	103.74(8)	O3−B1−O3^b	117.1(3)
Al−O4	1.8607(17)	O5−Al−O4^a	107.43(9)	O3−B2−O4^a	118.6(2)
Al−O2	1.8850(17)	O1−Al−O2	77.11(8)	O3−B2−O5^c	121.2(2)
B1−O2	1.358(4)	O1−Al−O4	96.79(8)	O4^a−B2−O5^c	120.2(2)
B1−O3(×2)	1.372(3)	O2−Al−O4^a	90.79(8)		
B2−O3	1.395(3)	O4−Al−O4^a	79.50(8)		
B2−O4^a	1.401(3)	O1−Al−O4^a	143.88(11)		
B2−O5^c	1.327(3)	O2−Al−O4	154.29(9)		

spectrum. Figure 3 shows the ^{27}Al 3Q-MAS NMR spectrum of PKU-6. The central band ($-^1/_2 \rightarrow {}^1/_2$) exhibits a complex pattern consisting of several overlapped peaks. However, the isotropic dimension of the two-dimensional spectrum unambiguously shows that there is only one Al site with an isotropic chemical shift of 34.6 ppm. The observed chemical shift is just between the Al octahedron (~0 ppm) and tetrahedron (~50 ppm) and thus can be attributed to 5-coordinated Al. For a square-pyramidal geometry, one expects a large electric field gradient at the central atom in comparison with other more spherical geometries, such as octahedron or trigonal bipyramid, which may result in a large quadrupolar coupling constant (C_Q). The observed C_Q of PKU-6 is about 4.2 MHz, which is larger than those observed in regular octahedral systems.[13] Largely because of the orientation dependence of the second-order quadrupolar interaction, the ^{27}Al MAS NMR spectrum of PKU-6 exhibits a complex pattern. The asymmetry parameter calculated from the MAS spectrum is about $\eta = 0.38$.

The bond valence sum (BVS) calculation (based on non-H sites) indicated that most of the atoms in PKU-6 have regular BVS values, i.e., 2.89 for Al, 3.03 for B1, 2.99 for B2, and nearly 2 for O atoms, except O1 (BVS = 1.22). As shown in Table 1, O1 is the only O atom that does not bond to B in the structure. It bridges to two Al atoms with an Al−O1 distance of 1.803(2) Å. A significantly low BVS value implies that O1 is bonded to a proton as a hydroxyl group. This hydroxyl group is characterized by a sharp IR absorption band at 3552 cm^{-1}, and a weight loss (exptl 3.95 wt %) at about 700 °C is observed on the thermogravimetric (TG) curve because of dehydration (calcd 4.0 wt %). Thus, the structural formula of PKU-6 can be expressed as $Al_2(OH)B_3O_7$. Additionally, a high-temperature X-ray powder diffraction shows that the framework of PKU-6 collapses at 700 °C and converses into a known condensed aluminoborate $Al_4B_2O_9$ (see the Supporting Information).

As shown in Figure 2b, the structure of PKU-6 contains one-dimensional, eight-ring channels along the *b* axis composed of four BO_3 triangles and four AlO_5 square pyramids. The size of the channel is relatively small if the van der Waals radius of O is considered (see the Supporting Information). The Brunauer−Emmett−Teller surface area (N_2) of the as-synthesized PKU-6 sample is about 3 m^2/g, indicating that N_2 molecules may not reside in the channels. However, the sample may adsorb a small amount of water molecules, as indicated by the weight loss (~1.2 wt %) at low temperature (<300 °C) (see the Supporting Information).

Although the composition of PKU-6 ($HAl_2B_3O_8$) is close to that of PKU-5 ($Al_4B_6O_{15}$), the structures are completely different. In PKU-5, Al atoms are all octahedrally coordinated and form a (10,3)-*a*-type octahedral framework by sharing edges,[3] while in PKU-6, the AlO_5 square pyramids form one-dimensional chains, which are further interconnected by B_3O_7, forming a pyramidal/triangular mixed framework. In practice, PKU-6 was often found as an impurity in the PKU-5 products. Noting that the anhydrous aluminoborate PKU-5 was synthesized at 350 °C, it is mysterious that the hydrated aluminoborate PKU-6 can only be obtained at higher temperature (400 °C).

In summary, PKU-6 represents an interesting framework structure that contains AlO_5 square pyramids. Generally, Al tends to adopt closo coordination, such as tetrahedron, octahedron, and trigonal bipyramid. An interesting example is the layered aluminophosphate UiO-5.[6c] The Al atom is octahedrally coordinated in as-synthesized UiO-15, including a coordinated water molecule. Sintering at 125 °C removes the water molecules, resulting in a square-pyramidal Al, but the layers were topologically retained. Further increasing the sintering temperature led to a tetrahedral Al. In PKU-6, the unsaturated square-pyramidal Al may originate from geometrical restriction. As indicated above, the bridged O atoms (both O3) on the B_3O_7 group are located just above the square basal plane of the Al pyramids. The rigid nature and steric factor of the B_3O_7 group prevent the formation of the sixth Al−O bond with O3 or with other resided molecules. Finally, although PKU-6 does not evidently show microporous behavior, it does provide useful information to understand the coordination behavior of Al atoms in various solid-state materials.

Acknowledgment. This project is supported by the National Nature Science Foundation of China (Grant 20221101).

Supporting Information Available: Crystallographic data in CIF format and powder X-ray diffraction refinement, atomic coordinates, IR, TGA/DTA, and X-ray diffraction patterns after high-temperature annealing. This material is available free of charge via the Internet at http://pubs.acs.org.

IC070073K

---

(12) Sheldrick, G. M. *SHELXS-97, Program for the solution of crystal structures*; University of Göttingen: Göttingen, Germany, 1997. Sheldrick, G. M. *SHELXL-97, Program for the refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.

(13) (a) Faucon, P.; Charpentier, T.; Bertrandie, D.; Nonat, A.; Virlet, J.; Petit, J. C. *Inorg. Chem.* **1998**, *37*, 3726−3733. (b) Mokaya, R.; Jones, W. *J. Mater. Chem.* **1999**, *9*, 555−561. (c) Temuujin, J.; MacKenzie, K. J. D.; Jadambaa, T.; Namjildorj, B.; Olziiburen, B.; Smith, M. E.; Angerer, P. *J. Mater. Chem.* **2000**, *10*, 1019−1023. (d) Moulin, I.; Stone, W. E. E.; Sanz, J.; Bottero, J. Y.; Mosnier, F.; Haehnel, C. *J. Phys. Chem. B* **2000**, *104*, 9230−9238.