

Synthesis and Structure of an Aluminum Borate Chloride Consisting of 12-Membered Borate Rings and Aluminate Clusters

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A new aluminum borate chloride (PKU-8) was synthesized in a flux of boric acid, and the structure was established using powder X-ray diffraction techniques. PKU-8 contains an unusual framework structure of a large cage consisting of 12-membered borate rings [B₁₂O₃₀] and aluminate octahedra clusters [Al₇O₂₄].

Borates are interesting materials that show profound optical¹ and catalytic² properties. B atoms can be either triangularly or tetrahedrally coordinated in borate, and additionally, they tend to form polyborate groups; thus, borates often adopt complex structures. Aluminoborates are particularly interesting because of the possible cationic porous frameworks proposed by Yu et al.¹ Recently, several new porous aluminoborates have been synthesized in a flux of boric acid and structurally characterized, such as PKU-1,^{2a} PKU-5,^{2b} and PKU-6;^{2c} the frameworks of these aluminoborates, however, are all neutral instead of cationic. Nevertheless, the frameworks of these aluminoborates are very unusual. In PKU-1 and PKU-5, for instance, the Al octahedra share edges, forming porous octahedral frameworks, which further share O atoms with the triangular borates, as if they are covered by borates. The framework in PKU-6, on the other hand, consists of AlO₅ square-pyramidal chains and B₃O₇ groups. The unusual square-pyramidal geometry of Al is largely due to the steric effect of the triangular polyborate groups. In this Communication, we report the synthesis and structure of a new aluminum borate chloride, [H₁₈Al₇B₁₂O₃₆]Cl₃, denoted as PKU-8, which contains a cagelike framework structure consisting of 12-

membered borate rings [B₁₂O₃₀] and 7-Al octahedra clusters [Al₇O₂₄]. To the best of our knowledge, this is the first example of an inorganic framework that is built by these unusual building units.

PKU-8 was synthesized in a 100 mL Teflon autoclave in a flux of boric acid at 200 °C for 5 days using H₃BO₃ (25 mmol), NaBO₂ (25 mmol), and AlCl₃·6H₂O (15 mmol) as the starting materials. The obtained solid was washed with distilled water (70 °C) to remove residual boric acid and then dried at 80 °C overnight. The product is a polycrystalline powder, and the phase purity was confirmed by powder X-ray diffraction. The reaction temperature and the H₃BO₃/NaBO₂ ratios (4:1–4:6) were all crucial for the formation of PKU-8; otherwise, other aluminoborates or amorphous products were obtained (see Figure S2 in the Supporting Information). Additionally, PKU-8 can only be obtained by using aluminum chloride hexahydrate as an aluminum source; other aluminum sources, such as nitrate and hydroxide, did not yield PKU-8 but other aluminoborates. ²⁷Al and ¹¹B magic angle spinning (MAS) NMR and IR spectra indicated that the Al atoms are exclusively in octahedral coordination, while the B atoms are coordinated in both triangular and tetrahedral geometries.³ The structure of PKU-8, crystallizing in a rhombohedral cell with *a* = 15.0613(1) Å and *c* = 14.0134(2) Å in space group *R*3̄, was established by the ab initio model (or simulated)-annealing technique using TOPAS⁴ and refined with the Rietveld method.⁵

There are 19 non-H atoms in the framework structure of PKU-8, i.e., 3 Al, 4 B, and 12 O atoms. All Al atoms (Al1, Al2, and Al3) are octahedrally coordinated with an average

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- (3) Chemical analysis was done using ICP and XPS. TGA-MS was carried out on a thermal analyzer (NETZSCH STA, 449C) equipped with a quadrupole mass spectrometer (Balzers MID), with a 37–839 °C working temperature range and a 10 °C/min heating rate, showing stepwise weight loss and evolution of HCl and water molecules. IR: 705, 853, 1018 (BO₄), 1183, 1349 (BO₃), 3269 (B-OH), 3490 (μ³-OH) cm⁻¹. ²⁷Al NMR: δ -1.2 (Al(H₂O)₆³⁺ standard) is typical for the octahedral Al³⁺. ¹¹B NMR shows two resonance signals, a singlet at δ -6.39 (BO₄) and a doublet at δ -15.75 and 3.46 (BO₃) (BF₃·Et₂O standard). ¹H NMR shows two signals at δ 7.4 and 5.2 (TMS standard).

- (4) TOPAS: *General Profile and Structure Analysis Software for Powder Diffraction Data*, version 2.1; Bruker AXS: Karlsruhe, Germany.

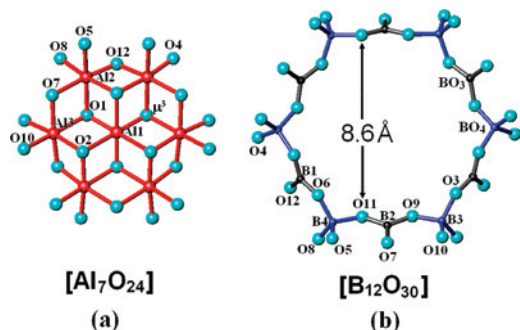


Figure 1. Fragments in PKU-8: (a) octahedral $[Al_7O_{24}]$ clusters; (b) 12-membered borate ring $[B_{12}O_{30}]$. Color code: Al, red; O, cyan; tetrahedral B, deep blue; triangular B, black.

Al–O distance of 1.995 Å for Al1, 1.948 Å for Al2, and 1.880 Å for Al3. The Al octahedra share edges, forming an Al octahedra cluster $[Al_7O_{24}]$ (Figure 1a). Al1 is the central octahedron that shares six edges with surrounding octahedra (Al2 and Al3). In fact, the $[Al_7O_{24}]$ cluster can be considered as a piece of layer in the brucite-type and the CoOOH structures.⁶ The B atoms are triangularly (B1 and B2) or tetrahedrally (B3 and B4) coordinated, with an average B–O distance of 1.35 Å for BO_3 groups and 1.45 Å for BO_4 groups. As shown in Figure 1b, the BO_3 and BO_4 groups are alternately linked, forming a large 12-membered borate ring $[B_{12}O_{30}]$. This is an unusually large and symmetric ring in the borate systems. The distance between the O atoms across the ring is about 8.6 Å, and, in addition, the terminal O atoms (O4, O5, O7, O8, O10, and O12) are all outward-pointed. In the framework structure of PKU-8, these terminal O atoms are shared with $[Al_7O_{24}]$ clusters, forming a 3D cage-like structure. Therefore, $[Al_7O_{24}]$ and $[B_{12}O_{30}]$ are the fundamental building units of the structure.

Figure 2a shows the framework structure of PKU-8. An easy way to understand the framework structure is to regard $[Al_7O_{24}]$ and $[B_{12}O_{30}]$ as large building units; thus, the framework of PKU-8 could be considered as a rock salt network, in which the $[B_{12}O_{30}]$ rings form ccp and the

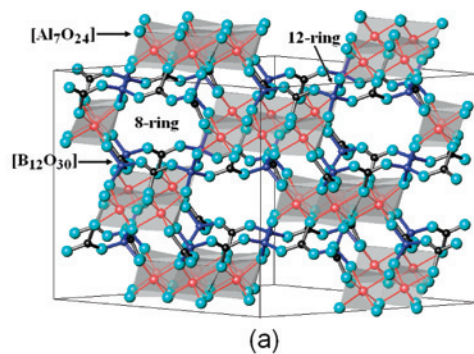


Figure 2. (a) Projection of the framework in PKU-8. Color code: Al, red; O, cyan; tetrahedral B, deep blue; triangular B, black. The Al octahedra are shaded. (b and c) Linkage of a $[B_{12}O_{30}]$ 12-membered ring and $[Al_7O_{24}]$ clusters.

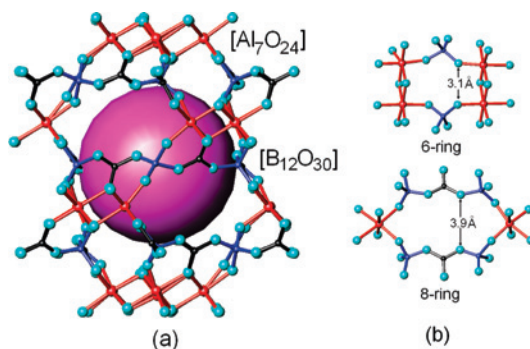


Figure 3. (a) Cavity and possible resident species in the structure. Color code: Al, red; O, cyan; tetrahedral B, deep blue; triangular B, black. The species in the cavity are expressed as large balls. (b) 6- and 8-membered rings interconnecting the cages.

$[Al_7O_{24}]$ fill in octahedral holes. Each $[B_{12}O_{30}]$ is linked with six $[Al_7O_{24}]$ via terminal O atoms and vice versa, just like Na and Cl in the rock salt structure. Regarding the complexity of the building units, it is fascinating that all of the terminal O atoms on $[B_{12}O_{30}]$ and $[Al_7O_{24}]$ can fit in such an exact way. As shown in Figure 1, both $[Al_7O_{24}]$ and $[B_{12}O_{30}]$ are hexagon-like species and, furthermore, every edge of the hexagons consist of three outward terminal O atoms (O4, O8, O12 and O5, O7, O10) that are perfectly shared between $[Al_7O_{24}]$ and $[B_{12}O_{30}]$ in the framework structure as shown in parts b and c of Figure 2. Such a linkage leads to notable 3-membered $[2B + Al]$ rings (Figure 2b,c), known as a preferred geometry for the porous aluminoborate frameworks.²

A remarkable feature of the framework structure of PKU-8 is the large ellipsoidal cages shown in Figure 3a. The ellipsoid is centered at the $[B_{12}O_{30}]$ 12-membered rings and capped by two $[Al_7O_{24}]$ clusters at the long ends. The cages are interconnected by 6-membered ($4AlO_6 + 2BO_4$) and 8-membered ($2AlO_6 + 4BO_4 + 2BO_3$) ring windows, as shown in Figure 3b. The sizes of the interconnected rings

(5) Crystallographic study. X-ray powder diffraction data were collected on a Bruker D8-Advance diffractometer with a curved germanium primary monochromator ($Cu K\alpha_1$) in a transmission mode (2θ range = 9–100°, step = 0.0144°, scan speed = 60 s/step, 50 kV, 40 mA) at room temperature. The diffraction pattern can be readily indexed to rhombohedral, $a = 15.0613(1)$ Å and $c = 14.0134(2)$ Å, and the possible space groups $R\bar{3}$, $R\bar{3}$, $R32$, $R3m$, or $R\bar{3}m$. The electron diffraction pattern confirms the rhombohedral setting of the structure (see the Supporting Information). The nonlinear optical effect (0.3, KDP as reference) of the powder sample rules out the centrosymmetric space groups. The structure model was initially established in the space group $R\bar{3}m$, in which the AlO_6 octahedron was used as a rigid fragment in the ab initio structural determination (TOPAS⁴). After several trial and errors, it became clear that Al atoms are all octahedrally coordinated in the $[Al_7O_{24}]$ cluster. The other O and B atoms were located by further structural refinement with the model-annealing method. The Rietveld refinement in $R\bar{3}m$ with the constrained isotropic displacement factors led to $R_p = 0.052$ and $R_{wp} = 0.078$. Further reducing the symmetry to $R\bar{3}$ significantly improved profile-fitting ($R_p = 0.040$, $R_{wp} = 0.056$, $R_B = 0.029$, and GOF = 3.42), while the fundamental framework remains unchanged. The residual electron densities within the cavity of the framework for an as-synthesized sample were attributed to chlorine ions and water molecules. The structural determination suggested a formula $[H_{18}Al_7B_{12}O_{36}]Cl_3$, $Z = 3$.

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are rather small; the shortest O–O distance is about 3.1 Å for the 6-membered ring and 3.9 Å for the 8-membered ring.

Including only the non-H atoms, the composition of the framework is $[\text{Al}_7\text{B}_{12}\text{O}_{36}]^{15-}$, $Z = 3$. The O atoms in the structure can be classified into four categories according to the linkage to Al and B. The terminal O atoms (O4, O5, O8, and O10) on the $[\text{Al}_7\text{O}_{24}]$ cluster are further linked to boron tetrahedra; they are two-coordinated O atoms. Other two-coordinated O atoms are those bridging to two B atoms (O3, O6, O9, and O11) in the $[\text{B}_{12}\text{O}_{30}]$ ring. The rest of the O atoms are all three-coordinated; O7 and O12 are bonded to two Al and one triangular B, while O1 and O2 are the μ^3 -O atoms that are capped on all three Al atoms in $[\text{Al}_7\text{O}_{24}]$. The bond valence sum (BVS) calculation reveals significantly low BVS values for two-coordinated O4, O5, O8, and O10 (average BVS ~ 1.37) and μ^3 -O1 and -O2 (average BVS ~ 1.25), while the rest are all close to 2. The O atoms with low BVS values should further bond to protons as OH groups. The presence of the OH groups is supported by IR bands at 3269 and 3490 cm^{-1} and two resonance peaks at 7.4 and 5.2 ppm in ^1H MAS NMR. Interestingly, similar μ^3 -OH groups were also observed in the brucite and CoOOH structures.⁶ Taking the possible protons into account, the framework composition of PKU-8 should be $[\text{H}_{18}\text{Al}_7\text{B}_{12}\text{O}_{36}]^{3+}$.

The cavities centered at the 12-membered borate rings are large ellipsoids of about 12 Å in length and 8.6 Å in diameter as shown in Figure 3a. However, the interconnected 6- and 8-membered ring windows are rather small. In addition, the protons on the framework may further reduce the size of cavity. The structural refinement on the as-synthesized sample reveals large residual electron densities from resident species within the ellipsoidal cavity. Owing to the mobility and possible random occupation of the resident species, it is difficult to assign all electron density peaks. However, the two highest residual peaks are definitely from the chlorine ions. Further considering the charge balance, the composition of PKU-8 should be $[\text{H}_{18}\text{Al}_7\text{B}_{12}\text{O}_{36}]\text{Cl}_3$.⁷ This formula agrees reasonably well with the results of chemical analyses (experimental, ICP, B:Al = 1.88:1; XPS, B:Al:Cl = 1.60:1:0.47; calculated, B:Al:Cl = 1.714:1:0.429).

The framework of PKU-8 retains up to 300 °C, above which the framework collapses as indicated by powder X-ray diffraction (see the Supporting Information). The adsorbed water can be completely removed up to about 250 °C without affecting the framework with a weight loss of about 4.8 wt % ($\sim 3\text{H}_2\text{O}$). At high temperature, a large and sudden weight loss occurs at about 400 °C (19.6 wt %), followed by a gradual weight loss up to 600 °C (3.2 wt %). The released gas species, monitored by mass spectroscopy, are water below 250 °C and HCl and water above 250 °C. The water molecules released at high temperature originate from dehydration of the hydroxyl groups of the framework, while

with the collapse of the cationic framework, the protons combine with the chloride anions to give off HCl. The calculated weight loss for the dehydration of OH and release of HCl is about 22.8 wt % based on the formula of $[\text{H}_{18}\text{Al}_7\text{B}_{12}\text{O}_{36}]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$, which coincides very well with the experimental results.

The framework in PKU-8 is less stable than those of the other known aluminoborates. As an anhydrous aluminoborate, the framework in PKU-5 is very stable (~ 800 °C),^{2b} while in hydrated aluminoborate PKU-1, the hydroxyl groups are bonded mostly to BO_3 as terminal OH groups, and thus its stability is also relatively high (~ 600 °C).^{2a} In PKU-8, the hydroxyl groups are bonded, respectively, to B on the BO_4 groups and as μ^3 -O to Al in the $[\text{Al}_7\text{O}_{24}]$ clusters. In comparison with the low decomposition temperature (300 °C) of aluminum oxyhydrate,⁸ one would expect that the infirm place of the PKU-8 framework might be the μ^3 -OH of the $[\text{Al}_7\text{O}_{24}]$ clusters.

In conclusion, PKU-8 represents an interesting framework structure that is built with two unusual building units, i.e., a 12-membered borate ring $[\text{B}_{12}\text{O}_{30}]$ and an Al octahedra cluster $[\text{Al}_7\text{O}_{24}]$, by sharing terminal O atoms. The framework contains a large ellipsoid cage centered at the 12-membered borate ring $[\text{B}_{12}\text{O}_{30}]$. However, because of small interconnected 8-membered ring windows, PKU-8 does not exhibit typical microporous behavior. Additionally, structural studies and BVS calculations show that the framework in PKU-8 is cationic ($[\text{H}_{18}\text{Al}_7\text{B}_{12}\text{O}_{36}]^{3+}$). The cationic frameworks have often been seen in organic–inorganic hybrid materials or coordination polymers⁹ but are rare for pure inorganic frameworks. For a few aluminoborate systems that were claimed as cationic framework materials,¹ no structural information has yet been reported. A curious question for cationic aluminoborates is how the low valence ions (Al^{III} and B^{III}) can form cationic frameworks. The structure of PKU-8 provides, at least, one possible interpretation, i.e., tightly bonded protons may compensate for the negative charge of the oxide framework. This observation may help us to understand the cationic behavior of previously reported aluminoborates. In fact, all of these materials exhibit low thermal stability, which is certainly the case if hydroxyl groups exist on the frameworks.

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Supporting Information Available: Crystallographic data, Rietveld refinement, IR spectrum, ^{11}B , ^{27}Al , and ^1H NMR spectra, X-ray patterns at different temperatures, and TGA/MAS data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(7) The formula $[\text{H}_{18}\text{Al}_7\text{B}_{12}\text{O}_{36}]\text{Cl}_3$ counts only the framework and the counter chlorine anions. The chemical analyses also indicated the presence of a small amount of Na ions in PKU-8, but the content varies for samples obtained under slightly different reaction conditions. The highest sodium content found in the PKU-8 samples is about Al:Na = 1:0.3.

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