

An Addition to the Oxoacid Family: $\text{H}_2\text{B}_{12}(\text{OH})_{12}$

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Received April 2, 2004

The acid $\text{H}_2\text{B}_{12}(\text{OH})_{12}$ can be isolated as a crystalline solid by protonation of the hydroxylated borane anion, $\text{B}_{12}(\text{OH})_{12}^{2-}$. This acidic compound has low solubility in water, conducts protons in the solid state, and has thermal stability to a temperature of 400 °C. The conductivity mechanism is a Grotthuss mechanism with a low activation enthalpy (9–13 kcal/mol). This new acid represents an addition to the class of oxoacids, of which sulfuric and phosphoric acid are the most prominent examples.

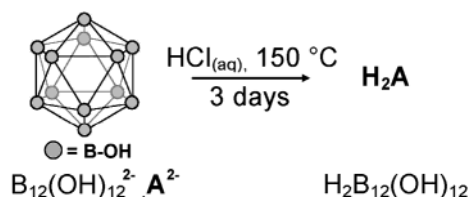


Figure 1. The $\text{B}_{12}(\text{OH})_{12}^{2-}$, A^{2-} , can be protonated readily to provide the conjugate acid, $\text{H}_2\text{B}_{12}(\text{OH})_{12}$, H_2A .

The acidic form of many oxoanions has been utilized in a wide range of applications, one of which is generation of proton conducting electrolytes. This class of electrolyte materials has been receiving much attention due to utility in fuel-cell and related energy storage systems¹ and exists as neat acids, polymer electrolytes,² and solid salts³ to name a few. New oxoanion based acid systems may have similar applications. Recent work^{4,5} has opened the way toward the use of polyhedral boranes and carborane anions as boron analogues of these common oxoanions through the synthesis of polyhydroxylated boranes and carboranes. The parent structure, $\text{B}_{12}(\text{OH})_{12}^{2-}$, A^{2-} , can be easily functionalized,^{6,7} yet one of the least complicated synthetic targets, the

conjugate acid of the hydroxylated dianion, H_2A , has not been reported (Figure 1). The H_2A compound, $\text{H}_2\text{B}_{12}(\text{OH})_{12}$, serves as a closer boron analogue of phosphoric and sulfuric acid than boric acid, $\text{B}(\text{OH})_3$, due to potential higher proton activity and lack of Lewis acidity. To this end, we report the synthesis and characterization of $\text{H}_2\text{B}_{12}(\text{OH})_{12}$.

It had been reported previously that treatment of aqueous solutions of $\text{B}_{12}(\text{OH})_{12}^{2-}$ with mineral acids produces an oxonium salt, $(\text{H}_3\text{O})_2\text{B}_{12}(\text{OH})_{12}$.^{4a} Comparison of this material with related oxonium and hydronium salts⁵ showed that the behavior of the A^{2-} framework was inconsistent with this formulation. In particular, thermal gravimetric analysis did not produce the expected mass loss upon decomposition to support oxonium formulation. The mass loss was variable and suggested that the acidic proton may exist as a hydrated oxonium such as the H_5O_2^+ cation.⁸

To test this hypothesis, structural characterization of the ambiguous oxonium salt prepared via literature methods was undertaken. Another cation system that would closely mimic the size and hydrogen bonding ability of the oxonium ion, the ammonium salt $(\text{NH}_4)_2\text{B}_{12}(\text{OH})_{12}$, was also studied for comparison purposes.^{4a} Both materials were examined by X-ray powder diffraction, and the data showed that, despite cation similarities, the two structures were dissimilar (Figure 2a and b). Indexing of the ammonium salt suggested that it was isostructural to the reported potassium salt.^{4a,9} Rietveld refinement using the $\text{K}_2\text{B}_{12}(\text{OH})_{12}$ structure as a starting model of the ammonium salt showed excellent agreement between data and model structure.^{10,11}

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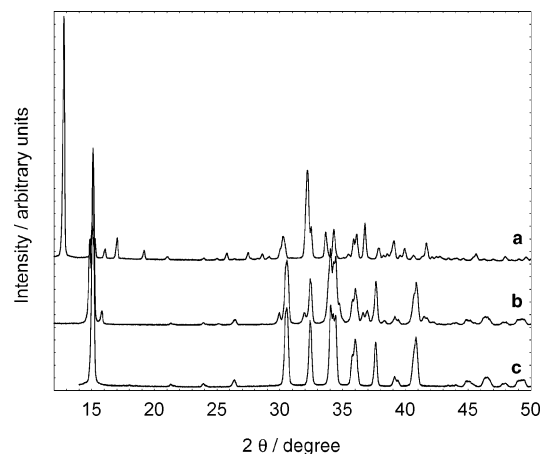


Figure 2. X-ray powder diffraction comparing $X_2B_{12}(OH)_{12}$ species from solution (a, $X = NH_4$, and b, $X = H$) and hydrothermal preparations (c, $X = H$).

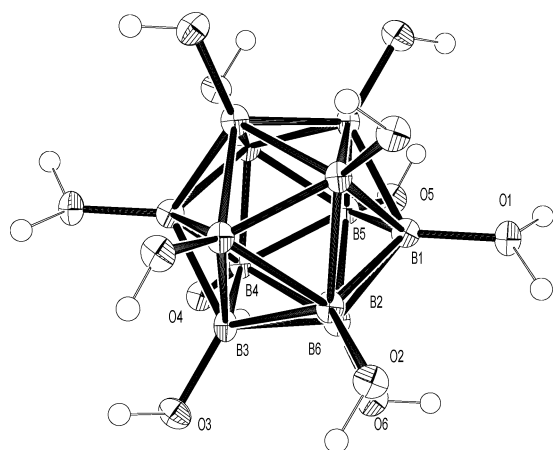


Figure 3. ORTEP (50% probability level) of $H_2B_{12}(OH)_{12}$.

The interpretation of the powder diffraction data and thermal characterization of the postulated hydronium salt of A^{2-} was complicated by heterogeneity in samples prepared via the literature methods. While the bulk of the material was consistently of a single microcrystalline phase, the presence of impurity phases hampered the structural identification of the powder. The low solubility complicated purification and prompted the utilization of a hydrothermal preparation to improve crystallinity. Allowing the cesium salt of A^{2-} to react in concentrated HCl at 150 °C and 125 psi in an acid digestion bomb for 3 days yielded a well-defined crystalline solid.¹¹ Several small crystals were selected for single-crystal X-ray analysis while the bulk sample was also measured by powder X-ray diffraction. Powder diffraction showed that the major component of the aqueous precipitation route was identical to the material obtained via hydrothermal synthesis (Figure 2b,c) Structural solution of single-crystal diffraction data (Figure 3) demonstrated that the material which was believed to be the

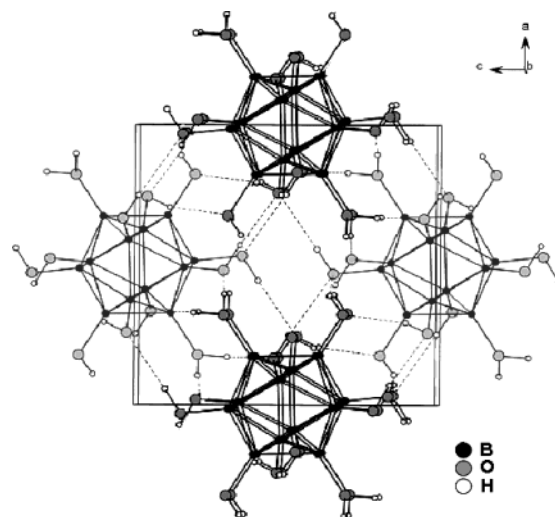


Figure 4. Hydrogen bonding of H_2A solid illustrating the 8 short hydrogen bonds (<2.6 Å O–O distance).

oxonium or hydronium salt was in fact the conjugate acid of the dianion, $H_2B_{12}(OH)_{12}$. The structural model generated from the single-crystal data could be used to fit the powder diffraction data illustrating that the structure was also representative of the bulk sample.

The conjugate acid does not show statistically significant differences within the intra-anion bond distances. Analysis of the reported structures of the monovalent cations for $X_2B_{12}(OH)_{12}$ ($X = H, Na, K, Rb, Cs$) shows that the average bond lengths of the B–B bonds in the hydroxylated cage are 1.795 Å with a standard deviation of 0.011 Å, and the B–O bonds are 1.446 Å with a standard deviation of 0.009 Å.^{4a} This variation can be attributed to the alkali metal salts having varying degrees of hydration which will in turn affect the Lewis acidity of the cation and the perturbation of the anion structure. Similarly, H_2A shows no bond elongation at the site of protonation (B–O bond distance 1.447(4) Å) even though it is formally an oxonium. This may be attributed to the acidic protons being involved in numerous short hydrogen bonds (<2.6 Å O–O distance) (Figure 4). There are 8 short hydrogen bonds per anion. Four originate at the protonated hydroxyl groups, acting as donors to four acceptor hydroxyl groups on different anions. This minimizes the structural effects on the anion upon protonation and may add to the observed thermal stability of the compound.

The H_2A material has excellent thermal stability, in excess of 400 °C in air or nitrogen, with less than 1% mass loss when heated in air at 300 °C for an extended period of time (1 h). Above 450 °C exothermic decomposition is observed. This stability may extend to reducing conditions as well due to the robust nature of the polyhedral borane and carborane frameworks and the high thermodynamic stability of the B–O bond, thereby circumventing some of the stability issues of the XO_4^{n-} ($X = S, Se, P$) anions.¹² The crystalline compound has very low water solubility,^{4a} which can be rationalized in light of the extensive hydrogen bonding seen in the solid state studies. This is in contrast to the behavior

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(11) See Supporting Information for complete characterization and synthesis information. H_2A : monoclinic, $P2_1/n$, $a = 8.2370(5)$ Å, $b = 8.2930(5)$ Å, $c = 8.3553(4)$ Å, $\beta = 90.143(2)^\circ$. Final R indices [$I > 2\sigma(I)$] $R1 = 0.0577$, $wR2 = 0.1395$.

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of hydronium salts of the structurally related mixed halo/hydroxyl carborane anions which show very high water solubility.⁵ The basicity of the anion is sufficient to fully accept protons from aqueous hydronium cations, which, when aided by favorable hydrogen bonding, leads to insolubility of **H₂A**. The extent of interaction of hydroxyl groups of the anion is also made evident by a number of sub van der Waals O–O contacts between the anions which are consistent with short–strong low barrier hydrogen bonding similar to what is seen in a number of proton bridged dimers.¹³ Additionally broad vibrational bands in the infrared spectrum of **H₂A** between 1600 and 1400 cm⁻¹ also support extensive, short, interanion H bonding that is in accordance with the structural studies.¹⁴

The conjugate acid is a stable, acidic solid well suited for proton conductivity in the solid state due to the extensive hydrogen bonding environment. The conductivity of iso-statically pressed pellets of the neat material was measured by impedance spectroscopy,¹⁵ and the pellets of the solid acid were found to have a conductivity of $1.5 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ at room temperature. This is an order of magnitude greater than proton conducting ionic salts such as CsHSO₄ at room temperature.¹⁶ For comparison, the NH₄⁺ salt was also examined and found to have a much lower conductivity at room temperature, $\sim 10^{-7} \Omega^{-1} \text{cm}^{-1}$. The conductivity values of the acid appear to vary with temperature and begin to *decrease* as a function of temperature until 60 °C where the conductivity begins to increase. Physisorbed water on the crystalline surface may be altering the conductivity at lower temperatures though thermal characterization (*vide supra*) shows no significant amounts of water associated with the crystalline compound, nor is there an observed phase change which could produce similar effects. Above 60 °C, the conductivity increases in an Arrhenius manner with an activation enthalpy between 9 and 13 kcal/mol. The activation enthalpy along with the structure is consistent with a Grotthuss (proton hopping) mechanism.¹⁷

Further evidence supporting a Grotthuss mechanism can be obtained from solid state ¹H NMR measurements. The spectrum of **H₂A** at 21 °C consists of 2 signals, a broad component and a narrower one which has a line width of 9.4 kHz. This is indicative of motional narrowing of the

acidic proton signal.¹⁸ The line widths and relative intensities of the two components vary with temperature. Variable temperature measurements and the use of a 2-site exchange model allow for the extraction of an activation enthalpy (~ 3 kcal/mol) for the exchange process which was found to be lower than obtained from conductivity measurement.^{18,19} This difference is likely the result of observation of two separate phenomena with each technique, intra-anion proton exchange and interanion proton migration. Above 60 °C, where the change in the conductivity behavior is observed, the solid state ¹H NMR measurements for **H₂A** show a constant spin–spin relaxation time indicating a change in proton dynamics accompanied by intensity transfer of the broad signal to the narrower one. Since spin–lattice relaxation of protons in the slow motion regime is dominated by dipole–dipole interactions, *T*₁ should decrease as the proton mobility increases.²⁰ In agreement with this, the spin–lattice relaxation times at 19, 65, and 104 °C are 57, 34, and 24 s respectively. These observations support that the conductivity is protonic with a high degree of proton motion among the anion hydroxyl groups and free exchange with the protons of the zwitterionic oxonium center. A more thorough study to characterize the nature of this proton migration is ongoing.

In conclusion, the conjugate acid H₂B₁₂(OH)₁₂ can be readily synthesized and has a range of useful properties including thermal stability and protonic conductivity. The acid material (or an analogue) has a wide range of potential applications due to similarity with well-known oxyacids. This work illustrates one small facet of the applicability of this type of system to areas currently dominated by traditional oxoanions.

CAUTION! *The functionalized polyhedral boranes and carboranes have been known to decompose violently in certain situations. While no sensitivity has been noted with the crystalline H₂B₁₂(OH)₁₂, produced via hydrothermal methods, powder samples from aqueous precipitation reactions have detonated mildly with an applied pressure > 10 ton/cm². Please exercise all due caution in the synthesis and handling of these materials.*

Acknowledgment. We greatly acknowledge Dr. Chen for his assistance with the collection of the single-crystal X-ray diffraction data. This material is based upon work supported in part by the U.S. Army Research Laboratory and the U.S. Army Research office under Grant DAAD19-03-1-0080.

Supporting Information Available: Complete synthesis and characterization including NMR, IR, powder and single-crystal diffraction data, and conductivity measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC049564K

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