

## Mixed halo/hydroxy carborane anions: thermally stable platforms for hydronium ion isolation†

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Hydroxylation of the robust, weakly coordinating hexahalo-carborane anion system,  $\text{CB}_{11}\text{H}_6\text{Br}_6^{-1}$ , produces a new class of anion with mixed halo/hydroxyl substituents,  $\text{HCB}_{11}(\text{OH})_5\text{Br}_6^{-1}$  which can be used to isolate a number of hydronium cation salts including an 'ice tautomer' composed of hydronium cation, anion hydroxyl groups and coordinated water molecules.

In recent years, weakly coordinating anions<sup>1</sup> (WCA) have been shown to be effective in isolating a wide range of reactive cations. In particular, anion systems based upon carborane anions such as the  $\text{CB}_{11}\text{H}_{12}^{-1}$  framework, have been shown to be near ideal platforms for the generation of a number of WCA systems, each with a particular niche where the properties of the anion have been matched towards specific synthetic challenges or where use of a WCA system alters reactivity.<sup>2</sup> Notable successes include the isolation of protonated arenes and superacidic Brønsted acids,<sup>3</sup> trivalent tin(III) cations,<sup>4</sup> 'non-classical' carbonyl complexes,<sup>5</sup> improved cationic catalysis,<sup>6</sup> and a series of protonated solvents<sup>7</sup> including a hydronium salt as the  $\text{H}_9\text{O}_4^{+1}$  cation.<sup>8</sup>

Hydronium salts are of interest because members of this class of compounds are known to act as solid-state proton conductors.<sup>9</sup> These materials do not exist as the free  $\text{H}_3\text{O}^+$  moiety, or oxonium ion, which is difficult to obtain except through the use of super acidic media.<sup>10</sup> More commonly the oxonium ion is coordinated by the anion or water molecules to form extended structures such as the  $\text{H}_5\text{O}_2^{+1}$ ,  $\text{H}_7\text{O}_3^{+1}$ , or  $\text{H}_9\text{O}_4^{+1}$ .<sup>11</sup> These represent successive coordination of water molecules to the oxonium to produce hydrated hydronium ions. Hydration or anion coordination can suppress the superacidity of the oxonium ion.<sup>12</sup> By tailoring the anion, we seek a series of hydronium salts which are stable, easily handled solids to study the structure, acidity and other properties of this fundamental cation system.

The hexabromo carborane anion,  $\text{CB}_{11}\text{H}_6\text{Br}_6^{-1}$ , can be converted to a mixed halo/hydroxy derivative,  $\text{HCB}_{11}(\text{OH})_5\text{Br}_6^{-1}$ ,  $\text{A}^{-1}$ , by adapting techniques that were first used to introduce hydroxyl groups to underivatized *closo*-boranes (Fig. 1).<sup>13</sup> Hydroxylation was accomplished by refluxing the caesium salt in 30% hydrogen peroxide. (Caution: Use of strong oxidants with the polyhedral boranes has led to explosive decomposition and formation of compounds that detonate. While no sensitivity was noted in this study, caution is warranted.) The reaction can be monitored *via* <sup>11</sup>B NMR and shows that substitution takes place solely at the 2–6 positions of the carborane cage, replacing the five

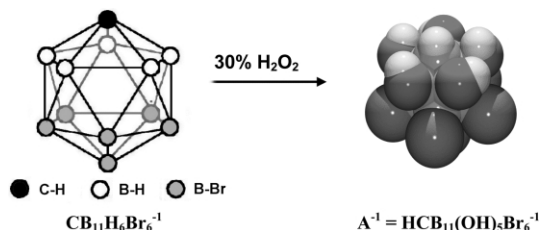


Fig. 1 Conversion of hexahalo-carborane anion into a mixed halo/hydroxy derivative.

† Electronic supplementary information (ESI) available: Synthesis and X-ray data and colour figures. See <http://www.rsc.org/suppdata/cc/b3/b314475e/>

B–H bonds with hydroxyl groups to produce the mixed halo/hydroxyl anion,  $\text{A}^{-1}$ , in high yield (77%). Metathesis of the cesium counterion with the methyl triphenyl phosphonium cation produces  $[\text{MePPh}_3^{+1}\text{A}^{-1}]$  (**1**, 60% overall). Crystals of **1** as a trihydrate were obtained from acetone–water and found suitable for X-ray diffraction. (Fig. 2) The effect of the high degree of hydroxylation manifests as extended interanion hydrogen bonding arrays as well as a number of hydrogen bonds to water solvates.<sup>14</sup> Compound **1** is quite soluble in polar and arene based organic solvents despite these interactions.

While the isoelectronic family of *closo*-borane derivatives  $\text{B}_{12}\text{H}_{12}^{-2}$ ,  $\text{CB}_{11}\text{H}_{12}^{-1}$ , and  $\text{C}_2\text{B}_{10}\text{H}_{12}$ , are rapidly hydroxylated (~6 h), the hexahalo anion,  $\text{CB}_{11}\text{H}_6\text{Br}_6^{-1}$ , was slow to react under similar conditions, undergoing complete substitution only after 48 h.<sup>13</sup> The increased stability of the halo-carborane is attributed to the masking effect of halogen substituents at the 7–12 positions of the carborane cage which are known to be more susceptible to electrophilic attack than the other positions of the boron cage. This stabilizing effect in the mixed halo/hydroxyl anion,  $\text{A}^{-1}$ , is illustrated by the fact that even extensive reflux in 30% hydrogen peroxide (with addition of additional hydrogen peroxide to replenish that which had undergone thermal decomposition) produces no new boron containing species in the reaction mixture even after a week. Undecahydroxycarborane,  $\text{HCB}_{11}(\text{OH})_{11}^{-1}$ , and dodecahydroxydodecaborane,  $\text{B}_{12}(\text{OH})_{12}^{-2}$  both decompose under these conditions.<sup>13</sup> The durability of the anion is also illustrated by stability towards acid and base. The caesium salt,  $\text{CsHCB}_{11}(\text{OH})_5\text{Br}_6$ , shows no decomposition when treated for 3 days in conc. sulfuric acid at 100 °C or when treated with 1 M NaOH at room temperature for 24 h. The mixed halo/hydroxy anion only begins to undergo decomposition after 6 h in 2 M NaOH at 100 °C.

The halo/hydroxyl anion offers a compromise in solubility between the halogenated and hydroxylated carborane/borane anions.<sup>14,13</sup> Solutions of the caesium salt,  $\text{Cs}^{+1}\text{A}^{-1}$ , up to 0.7 M can be obtained in water at room temperature. Solubility in polar, hydrogen bonding solvents such as methanol or acetonitrile (~0.1 M) is less than with unhydroxylated anions (0.5–1 M) but much greater than the fully hydroxylated carborane and borane anions whose caesium salts have negligible solubility in these solvents.

Passing the caesium salt through an acidic ion-exchange resin (Amberlyst-15) produces aqueous hydronium ion solutions of the mixed halo/hydroxyl carborane,  $\text{A}^{-1}$ . This solution can be

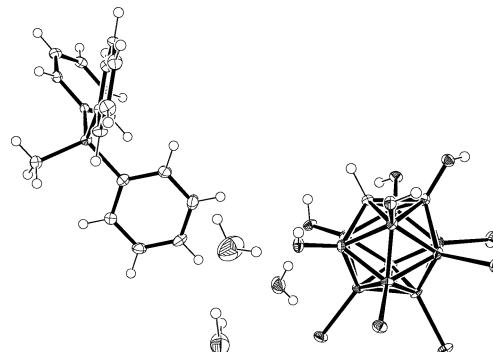
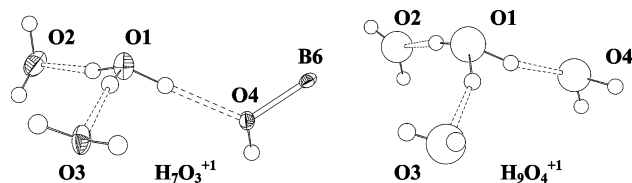


Fig. 2 Thermal ellipsoid plot (50%) of  $\text{MePPh}_3 \text{HCB}_{11}(\text{OH})_5\text{Br}_6 \cdot 3\text{H}_2\text{O}$ , **1**, from acetone–water.

processed at room temperature to generate a hygroscopic white solid which spectroscopic and thermal characterisation confirms as a  $\text{H}_3\text{O}^{+1} \cdot n\text{H}_2\text{O}$  ( $n = 3\text{--}5$ ) salt of  $\text{A}^{-1}$ , **2**. The acidic salt is a mixture of hydrated hydronium ions, the composition of which depends upon evaporation conditions.

The acidic material **2** can be transformed into the well defined  $\text{H}_5\text{O}_2^{+1}$  salt, **3**, by heating under vacuum at  $80^\circ\text{C}$ . The characteristic strong IR adsorption of the OH stretch of the  $\text{H}_5\text{O}_2^{+1}$  cation at  $3530\text{ cm}^{-1}$  along with the broad O–H–O vibration at  $\sim 1600\text{ cm}^{-1}$  indicate the presence of the proton bridged dimer.<sup>7</sup> This material is thermally stable until  $150^\circ\text{C}$  before water loss is observed. Unlike the hexahalocarboranes, the new anion system does not undergo acid promoted HBr loss below  $350^\circ\text{C}$  in the presence of the strongly acidic hydronium ion.<sup>8</sup>

A mixed salt can be formed by treating the  $\text{MePPh}_3^{+1}$  salt with dilute sulfuric acid and allowing the mixture to stand for several days which deposits long needles of a compound that was structurally characterized as  $[\text{H}_7\text{O}_3^{+1}, \text{MePPh}_3^{+1}]$  ( $\text{HCB}_{11}(\text{OH})_5\text{Br}_6^{-1} \cdot 3\text{H}_2\text{O}$ , **4**). In the solid state, the mixed salt **4** shows the hydronium cation interacting with a single hydroxyl group of the carborane cage. While the hydrogen atoms were modelled in the refinement, the O–O bond distances of  $2.498(4)\text{ \AA}$ ,  $2.577(4)\text{ \AA}$  and  $2.603(4)\text{ \AA}$  are clear indicators of hydronium cation character (Fig. 3, Table 1).<sup>7</sup> The overall geometry of the hydronium ion is similar to that of the previously reported  $\text{H}_9\text{O}_4^{+1}$  cation.<sup>8</sup> One feature of note is that the closest contact to the oxonium center is to a water molecule, not a hydroxyl group of the negatively charged anion. The O–O separation between the anion and the oxonium ion ( $2.604(5)\text{ \AA}$ ) is largest of the three coordinated species. The apparent lower basicity of the anionic B–O–H moiety compared to water reflects the extensive delocalization of charge on the carborane anion.



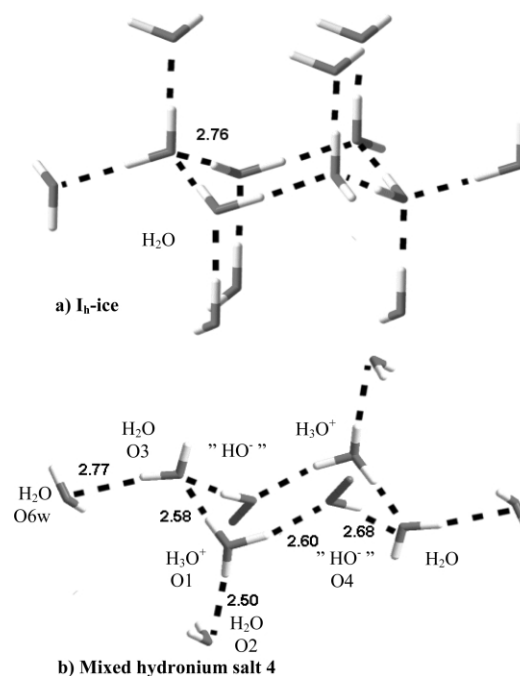
**Fig. 3** Comparison of the geometry of the  $\text{H}_7\text{O}_3^{+1}$  cation (from compound **4**) with the previously reported  $\text{H}_9\text{O}_4^{+1}$  cation.<sup>8</sup>

**Table 1** Hydronium ion geometry comparison

O–O dist./ $\text{\AA}$	$\text{H}_7\text{O}_3^{+1}$	$\text{H}_9\text{O}_4^{+1}$
O1–O2	2.498(4)	2.50(2)
O1–O3	2.577(4)	2.50(2)
O1–O4	2.603(4)	2.53(2)
<b>O–O–O angle/<math>^\circ</math></b>		
O2–O1–O3	112.55(15)	103.4(8)
O3–O1–O4	99.23(13)	117.0(8)
O4–O1–O2	126.22(12)	104.0(8)

Examination of the hydrogen bonding network of the charged species in the crystal lattice shows a cluster of  $\text{H}_7\text{O}_3^{+1}$  ions, anion hydroxyl groups, and weakly bound water molecules. This combination of features produce an overall structure reminiscent of a hydrogen bonding array of hexagonal ice,  $\text{I}_h\text{-ice}$  (Fig. 4).<sup>15</sup> The alternation of the oxonium ion, anion hydroxyl groups and neutral waters in the chair conformation can be seen as an ‘ice tautomer’. This one-dimensional hexagonal-ice analogue stretches throughout the crystal along the  $a$ -axis. This axis is the fastest growing axis of the crystal which suggests that the hydronium ion interaction leads to an enhancement of crystallization along the hydrogen bonding network.

In summary, modification of the already stable hexahalo carborane anion system produces a second generation anion that combines features of the hexahalo carborane with the per-hydroxylated borane anions. Of note is high thermal stability of the anion in the presence of hydronium ions, illustrated by the absence



**Fig. 4**  $\text{I}_h\text{-ice}$  vs. hydronium salt **4**. O–O distances shown in  $\text{\AA}$ .

of anion decomposition even to temperatures as high as  $350^\circ\text{C}$ . The hydroxylated framework provides a platform which can be used to stabilize and isolate a number of hydronium ions. A novel ‘ice tautomer’ can be formed which takes advantage of the hydrogen bonding ability of the anion during interactions with hydronium ions.

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- Compound **1**: Monoclinic,  $P2_1/c$ ,  $a = 9.3276(9)\text{ \AA}$ ,  $b = 13.2367(14)\text{ \AA}$ ,  $c = 28.181(3)\text{ \AA}$ ,  $\beta = 92.954(2)^\circ$ , Final  $R$  indices [ $I > 2\sigma(I)$ ]  $R1 = 0.0363$ ,  $wR2 = 0.0639$ . Compound **4**: Triclinic  $P1$ ,  $a = 9.4151(4)\text{ \AA}$ ,  $b = 15.5563(7)\text{ \AA}$ ,  $c = 19.8434(9)\text{ \AA}$ ,  $\alpha = 99.3420(10)^\circ$ ,  $\beta = 102.0120(10)^\circ$ ,  $\gamma = 95.3940(10)^\circ$ . Final  $R$  indices [ $I > 2\sigma(I)$ ]  $R1 = 0.0299$ ,  $wR2 = 0.0682$ .
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