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Pairing Heterocyclic Cations with *closo*-Icosahedral Borane and Carborane Anions. I. Benchtop Aqueous Synthesis of Binary Triazolium and Imidazolium Salts with Limited Water Solubility

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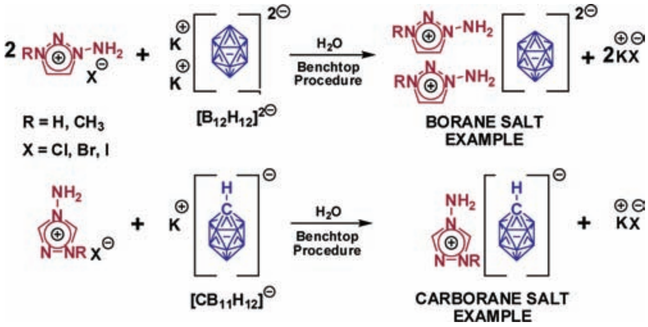
ABSTRACT



Ten new salts that pair triazolium and imidazolium cations with *closo*-icosahedral anions $[B_{12}H_{12}]^{2-}$ and $[CB_{11}H_{12}]^{-}$ were synthesized in water solvent using an open-air, benchtop method. These unreported [Heterocyclium]$_2$[$B_{12}H_{12}$] and [Heterocyclium][$CB_{11}H_{12}$] salts extend reports of [Imidazolium][$CB_{11}H_{12}$] and [Pyridinium][$CB_{11}H_{12}$] salts that were synthesized in anhydrous organic solvents under an inert atmosphere with glovebox or Schlenk techniques. Spectroscopic data, melting points, and densities are reported for each salt. Single-crystal X-ray structures are provided for the five new $[B_{12}H_{12}]^{2-}$ salts.

Tailoring the chemical and physical properties of molecular materials by rational design to increase density, reduce toxicity, or to improve overall stability characteristics continues to be an important research endeavor. Achieving this by the structural modification of neutral organic compounds offers a limited scope of opportunities. Organic-like solid and liquid salts significantly enhance this flexibility for tailoring properties by pairing different classical heterocyclic cations with a plethora of different counteranions. Over the past 25 years, this is re-emphasized with salts based on neutral heterocyclic compounds. Rekindled interest in this approach appears to initiate with the unique properties exhibited by the hygroscopic binary 1-Ethyl-3-methyl-1,3-imidazolium (EMIM) chloroaluminate salt[1] followed by a subsequent report of nonhygroscopic, air stable, binary

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EMIM salts containing other anions.[2] Later, triazolium cations are used to form salts with common anions.[3]

We now report the synthesis and characterizaton of salts containing heterocyclic cations that are paired with two different three-dimensional polyhedral borane/carborane anions,[4] $[B_{12}H_{12}]^{2-}$ and $[CB_{11}H_{12}]^{-}$, as well as a new aqueous preparation method that does not require air-free techniques. These unique salts are comprised of aromatic planar π-delocalized cations and aromatic polyhedral σ-delocalized anions. Triazolium and imidazolium cations paired with the *closo*-icosahedral, weakly nucleophilic $[B_{12}H_{12}]^{2-}$ dianion represent the first reported examples of these borane salts **1**−**5**.

The $[B_{12}H_{12}]^{2-}$ dianion, first synthesized in 1960 as the triethylammonium salt,[5] is known to form salts of low toxicity and high thermal stability[6] and is purported to be the most stable covalently bonded chemical entity in all of chemistry.[7a] It is a "super-aromatic" polyhedral-shaped "counterpart of the planar benzene molecule with 26 delocalized valence electrons in its σ-bonded framework"[7] and possesses an overall negative two charge. This unique $[B_{12}H_{12}]^{2-}$ dianion is paired with either two planar aromatic triazolium or two imidazolium cations, which each possess six delocalized valence electrons in its π-bonded cyclic structure and an overall positive one charge. These new $[\text{Heterocyclium}]_2[B_{12}H_{12}]$ salts **1**−**5** previously have not been reported. The icosahedral monoanion, *closo*-$[CB_{11}H_{12}]^{-}$, first reported in 1967,[8] also forms thermally stable salts. Analogous $[\text{Triazolium}][CB_{11}H_{12}]$ **6**−**9** and one new $[\text{Imidazolium}][CB_{11}H_{12}]$ **10** salts also are described which extend properties characterization beyond several $[\text{Imidazolium}][CB_{11}H_{12}]$[9] and one [Pyridinium] $[CB_{11}H_{12}]$[10] salts that previously were reported.

The former $[\text{Imidazolium}][CB_{11}H_{12}]$ salts were prepared by stirring the Cs^{+} or Ag^{+} salt of $[CB_{11}H_{12}]^{-}$ with the appropriate imidazolium halide in an *anhydrous organic solvent, or mixture of solvents, inside an inert-atmosphere glovebox* for 10 h. The solid phase CsCl or AgCl byproduct was separated from the supernatant by filtration through Celite. Removal of solvent afforded white crystals.[9] The [*N*-Pentylpyridinium]$[CB_{11}H_{12}]$ salt was *prepared similarly over 20 h using Schlenk air-free techniques* and column chromatography purification.[10]

In contrast, this first paper describes heterocyclium borane/carborane salts that are relatively water insoluble at rt where a high water solubility of the potassium halide byproduct is advantageous. Our aqueous-based metatheses require reaction times of only several minutes and are conducted in a benchtop fumehood with standard glassware open reaction vessels and deionized (DI) water solvent. With the relatively low water solubilities exhibited by the heterocyclium salts of $[B_{12}H_{12}]^{2-}$ **1**−**5** and $[CB_{11}H_{12}]^{-}$ **6**−**11**, anhydrous solvents can be avoided and air-stable products obtained. Because all the heterocylium halides used in this work, as well as the $K_2[B_{12}H_{12}]$ and $K[CB_{11}H_{12}]$ reactant salts,[11] are water-soluble, reactions are rapid. The two reagents are mixed in stoichiometric amounts, and precipitation or slow recrystallization yields the desired salt product **1**−**11**[12] which are readily separated from the potassium halide-containing aqueous supernatant by filtration and washing with cold DI water. Crude product yields are in the 71% to 96% range. Recrystallization from hot DI water, in some cases containing a small proportion of methanol, removes any small amounts of potassium and halide ions to give overall yields ranging from 44% to 84%. A trace of the residual potassium cation should not afford the catalysis problems sometimes caused by trace silver cations following a silver salt metathesis.

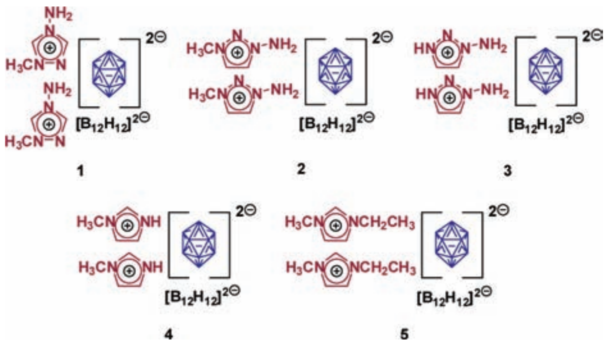

Figure 1. $[\text{Heterocyclium}]_2[B_{12}H_{12}]$ borane salts prepared.

Figure 1 displays the five heterocyclinium borane salts syntheszied by our benchtop, open-air, aqueous procedure. The synthesis and spectroscopic data for [4-Amino-1-methyl-1,2,4-triazolium]$_2[B_{12}H_{12}]$ **1** are typical.[13] More detailed syntheses for **1** and for the four other $[B_{12}H_{12}]^{2-}$ salts, 1-Amino-3-methyl-1,2,3-triazolium borane **2**, 1-Amino-3-H-1,2,3-triazolium borane **3**, 1-Methylimidazolium borane **4**, and 1-Ethyl-3-methylimidiazolium borane **5**, appear in the Supporting Information.

Figure 2 shows the six new $[\text{Heterocylium}][CB_{11}H_{12}]$ salts synthesized, 4-Amino-1-H-1,2,4-triazolium carborane **6**, 4-Amino-1-methyl-1,2,4-triazolium carborane **7**, 1-Amino-3-methyl-1,2,3-triazolium carborane **8**, 1-Amino-3-H-1,2,3-triazolium carborane **9**, 1-Methylimidazolium carborane **10**, and 1-Ethyl-3-methylimidazolium carborane **11**. The synthesis of **[**1-Amino-3-H-1,2,3-triazolium]$[CB_{11}H_{12}]$ **9** is typi-

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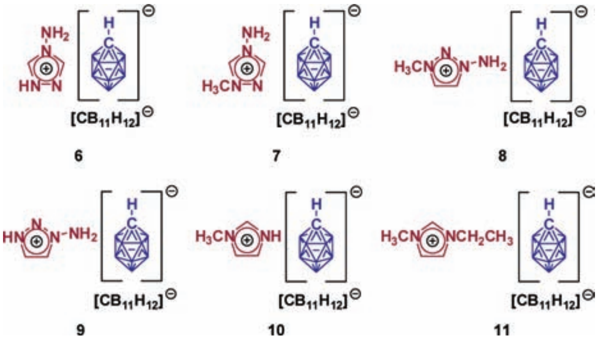

Figure 2. [Heterocyclium][$CB_{11}H_{12}$] carborane salts prepared.

cal.[14] More detailed [Heterocyclium][$CB_{11}H_{12}$] salt syntheses for salts **6**−**11** appear in the Supporting Information.

Initial syntheses were conducted on a small 150−200 mg scale based on $K_2[B_{12}H_{12}]$ and $K[CB_{11}H_{12}]$. Once optimum conditions were determined for each salt, the metathesis reactions were conducted on a 1−4 g scale. The $[B_{12}H_{12}]^{2-}$ salt of **3** was directly scaled from 2 to 5.5 g for $K_2[B_{11}H_{12}]$ with a comparable yield and final purity.

The density, melting point, and reaction yields for salts **1** to **11** are listed in Tables 1−3. Experimental densities are obtained by pycnometry at rt and are compared to a newly developed predictive density additivity code[15] that initially was updated for heterocyclium *closo*-icosahedral borane and carborane salts. This updated code predicts an average 2.0% variance from the 11 pycnometry-based density values. Density differences range from 4.2% with salt **6** to 0% with salts **7** and **9**. Pycnometry densities for salts **2** and **3** do not contain occluded solvent molecules which are present in the single crystal X-ray analyses.[16]

Table 1. 4-Amino-1,2,4-Triazolium Borane and Carborane Salts

 n	 $[B_{12}H_{12}]^{2\ominus}$ n = 2	 $[CB_{11}H_{12}]^{\ominus}$ n = 1	melting point (°C) density (g/cc) pychnometry / x-ray (predicted)	yields (%) direct ppt. (Overall)
1: X = CH_3	Borane	–	181−182 1.22/1.24 (1.20)	91.0 (79.7)
6: X = H	–	Carborane	260−262 1.19/– (1.14)	71.0 (43.5)
7: X = CH_3	–	Carborane	161−162 1.12/– (1.12)	92.0 (65.5)

Table 2. 1-Amino-1,2,3-Triazolium Borane and Carborane Salts

 n	 $[B_{12}H_{12}]^{2\ominus}$ n = 2	 $[CB_{11}H_{12}]^{\ominus}$ n = 1	melting point (°C) density (g/cc) pychnometry / x-ray (predicted)	yields (%) direct ppt. (overall)
2: X = CH_3	Borane	–	199−218[a] 1.19/1.13[16] (1.18)	78.2 (66.7)
3: X = H	Borane	–	148−152[a] 1.26/1.27[16] (1.27)	76.4 (61.1)
8: X = CH_3	–	Carborane	259−262 1.10/– (1.14)	95.8 (76.5)
9: X = H	–	Carborane	182−183[a] 1.16/– (1.16)	70.8 (54.9)

[a] Melts with gas evolution.

An X-ray crystal packing structure of [4-Amino-1-methyl-1,2,4-triazolium]$_2$[$B_{12}H_{12}$] **1** appears in Figure 3. Single

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(11) The $K_2[B_{12}H_{12}]^{2-}$ and $K[HCB_{11}H_{11}]^{-}$ reactants were purchased from Katchem Ltd., E. Krasnohorske 6, 110 00 Prague 1, Czech Republic and were used as received.

(12) Depending upon the salt product solubility, some heterocyclium salts immediately precipitate; in other cases, the desired heterocyclium salt crystallizes overnight at +3.5 °C.

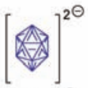
(13) [4-Amino-1-methyl-1,2,4-triazolium]$_2$[*closo*-$B_{12}H_{12}$], **1**: Solid [4-Amino-1-methyl-1,2,4-triazolium] iodide (4.52 g; 20.00 mmol), CH_3I methylated plus recrystallization from methanol) and commercial K_2[*closo*-$B_{12}H_{12}$] (2.20 g; 10.00 mmol) were placed into a 50 mL beaker. To this was added 18.0 mL DI water. The contents were stirred and heated at gentle reflux for 4 min. The resulting clear tan solution was cooled overnight in a refrigerator and off-white crystals deposited. Filtration and rinsing the filter-cake with 2 × 1.0 mL portions of pre-chilled DI water followed. The crystals were dried under high vacuum to give anhyd spectroscopically pure salt product by 1H NMR (3.096 g; 91.05%). Recrystallization of a portion (1.04 g) was conducted in 40.0 mL boiling DI water containing 5 mL anhydrous methanol. Most of the methanol boiled off. The resulting clear solution was cooled overnight in a refrigerator (3.5 °C) to give nicely formed crystals. Filtration, washing the crystals with 0.5 mL of pre-chilled DI water, and drying at 65 °C under high vacuum (50 mTorr) in a Chem-Dry apparatus over 72 h gave 0.91 g white solid; (recrysallized portion = 87.6% recovery); overall purified yield = 79.7%): ^{1}H NMR 400 MHz, std. DMSO-d_6 (2.51): δ 10.04 (s, 2H), 9.15 (s, 2H), 6.92 (s, 4H), 4.04 (s, 6H), 1.70−0.10 (complex m, 12H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (39.51): δ 145.05, 142.92, 38.97; FTIR (HATR) 3350, 3309, 3252, 3220, 3134, 3093, 2978, 2472, 2447, 1585, 1479, 1462, 1442, 1254, 1201, 1164, 1123, 1062, 988, 882, 850, 792, 711, 657, 621, 600, 568 cm^{-1}; X-ray in Figure 3 and Supporting Information.

(14) [1-Amino-3-H-1,2,3-triazolium][*closo*-$CB_{11}H_{12}$], **9**: Solid [1-Amino-3-H-1,2,3-triazolium] chloride (2.41 g; 20.00 mmol) and commercial K[*closo*-$CB_{11}H_{12}$] (3.64 g; 20.01 mmol) are placed into a 50 mL Pyrex beaker. Addition of 10.0 mL DI water was followed by heating to gentle reflux and then pouring the nearly clear solution into a fresh 50 mL Pyrex beaker leaving behind a small amount of a water insoluble impurity in the $K[CB_{11}H_{12}]$ reactant. The reaction mixture was cooled overnight in the refrigerator (3.5 °C) to effect crystallization. Filtration, rinsing the filter-cake with 2.0 mL of pre-chilled DI water, and pumping at high vacuum (60 mTorr) gave a 4.59 g of solid with some entrained water. Two recrystallizations from 7.0 mL refluxing DI water gave 2.51 g of pure salt; overall purified yield (two recrystallizations) = 54.9%): ^{1}H NMR 400 MHz, std. DMSO-d_6 (2.50): δ 8.71 (brs, 3H), 7.96 (d, J = 1.1 Hz, 1H), 7.74 (d, J = 1.1 Hz, 1H), 2.39 (brs, 1H), 2.25−0.75 (complex m, 11H); ^{13}C NMR (100 MHz, std. DMSO-d_6 (39.51): δ 132.09, 124.28, 50.79; FTIR (HATR) 3714, 3694, 3653, 3636, 3346, 3264, 3154, 3134, 2521, 1659, 1605, 1540, 1462, 1442, 1299, 1168, 1111, 1078, 1017, 956, 890, 788, 711, 694, 657, 625, 600, 564, 543 cm^{-1}; HRMS calcd for $[M - 3H]^-$ m/z = 225.2315, found 225.2325; calcd for $[CB_{11}H_{12}]^-$ m/z = 143.2035, found 143.2045.

(15) Ammon, H. L. *Propellants, Explos., Pyrotech.* **2008**, *33*, 92.

(16) Preparing acceptable single crystals for X-ray analysis results in two occluded CH_3CN molecules for salt **2** and two occluded H_2O molecules for salt **3**. Both salts become amorphorus powders when the solvent molecules are removed for pycnometry density analyses.

Table 3. Imidazolium Borane and Carborane Salts

 n	 $[B_{12}H_{12}]^{2-}$ n = 2	 $[CB_{11}H_{12}]^{-}$ n = 1	melting point (°C) density (g/cc) pychnometry / x-ray (predicted)	yields (%) direct ppt. (overall)
4: X = CH_3 Y = H	Borane	–	260–262[a] 1.08/1.11 (1.12)	82.3 (60.0)
5: X = CH_3 Y = CH_2CH_3	Borane	–	290–292[a] 1.06/1.10 (1.08)	81.6 (74.2)
10: X = CH_3 Y = H	–	Carborane	368–369[a] 1.11/– (1.07)	93.2 (83.5)
11: X = H Y = CH_2CH_3	–	Carborane	175–176[a,17] 1.03/– (1.05)	93.6 (69.5)

[a] Melts with gas evolution.

crystal X-ray data for [Heterocyclium]$[B_{12}H_{12}]$ salts **1**–**5** are found in the Supporting Information.[16] Melting points are obtained in open capillary tubes and are uncorrected. Both the crude and overall product yield are given for each salt in Tables 1–3. This overall yield is determined by multiplying the crude yield percent with the percentage of salt product recovered after recrystallization.

The previouly reported [1-Ethyl-3-methylimidazolium]-$[CB_{11}H_{12}]$ salt **11** was synthesized by a silver salt-based metathesis procedure.[9] The earlier measured X-ray single crystal density of 1.07 g/cm^3 compares well with our pycnometry density of 1.03 g/cm^3, taken at rt, and the predicted density[15] of 1.05 g/cm^3 (Table 3). Our visually determined melting point (1 °C/min) is 175–176 °C compared to the reported DSC-based melting point of 122 °C.[9] Apparently, an endothermic DSC peak at 122 °C was taken to be a melting point.[17] Our yields of 94% (crude), 74% (recrystallized), and 70% (overall) compare favorably with the 90% yield previously reported for salt **11**.[9]

The [4-Amino-1H-1,2,4-triazolium]$_2[B_{12}H_{12}]$ salt, analogous to $[CB_{11}H_{12}]^-$ salt **6**, is absent from Table 1. Unique challenges surfaced in its synthesis. Treating it like water-soluble binary triazolium and tetrazolium borane/carborane salts encountered in this research effort was the answer. These will be reported in a future publication as well as an option for pairing equimolar amounts of two dissimilar heterocyclic cations with the $[B_{12}H_{12}]^{2-}$ dianion to give mixed heterocyclium borane salts. Initial results have given three such mixed cation borane salts: e.g. [4-Amino-1-methyl-1,2,4-triazolium][1-Ethyl-3-methylimidazolium]$[B_{12}H_{12}]$ using the heterocyclic cations seen in salts **1** and **11**.

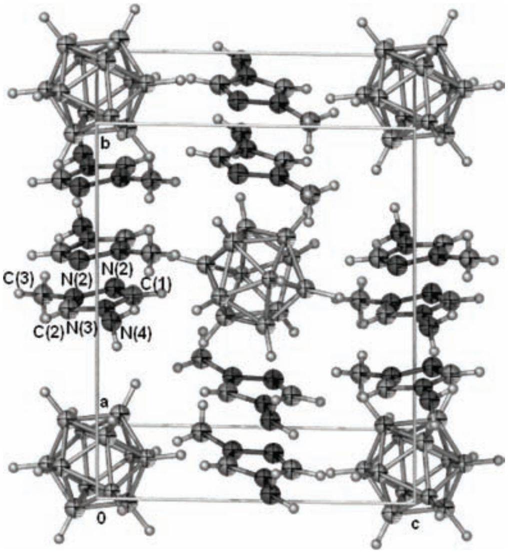


Figure 3. Crystal packing of salt **1** viewed along the crystallographic *a*-axis.

Acknowledgment. Mr. Milton B. McKay verified the ion chromatography halide ion content procedure prior to it being used for our Cl$^-$ analyses on salts **1**–**11.** AFRL/RZS, Edwards AFB, CA, provided administrative, financial, and technical support.

Supporting Information Available: Experimental procedures, textual spectroscopy data, detailed melting point notes, and ion chromatography Cl$^-$ analyses for salts **1**–**11**, DSC scans for salt **11**, single crystal X-ray for salts **1**–**5**, and HRMS for salts **6**–**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Our DSC analyses of salt **11** (1 °C/min) show a small endotherm at 128 °C, which we attribute to a solid phase transition, and a larger endotherm at 175–176 °C. This latter temperature matches the visually-determined melting point where a white solid changes to a colorless liquid. Visually-determined solid softening occurs from 106–132 °C.