

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 03-03-2009		2. REPORT TYPE Journal Article		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Pairing Heterocyclic Cations with <i>closo</i> -Icosahedral Borane and Carborane Anions. I. Benchtop Aqueous Synthesis of Binary Triazolium and Imidazolium Salts with Limited Water Solubility (Postprint)				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Scott A. Shackelford & Jerry A. Boatz (AFRL/RZSP); John L. Belletire, Stefan Schneider, & Amanda K. Wheaton (ERC), Herman L. Ammon (University of Maryland); Steven H. Strauss (Colorado State Univ.)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 50260541	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZSP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-RZ-ED-JA-2009-069	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZS 5 Pollux Drive Edwards AFB CA 93524-70448				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-RZ-ED-JA-2009-069	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited (PA #09117).					
13. SUPPLEMENTARY NOTES Published in <i>Org. Lett.</i> , 2009 , 11 (12), pp 2623–2626. Copyright © 2009 American Chemical Society					
14. ABSTRACT 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 properties tailoring 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 non-hygroscopic, air stable, binary EMIM salts containing other anions. ² Later, triazolium cations are used to form salts with common anions. ³ We now report the synthesis and characterization of salts containing heterocyclic cations that are paired with two different three-dimensional polyhedral borane/carborane anions, [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.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 5	19a. NAME OF RESPONSIBLE PERSON Dr. Scott A. Shackelford
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) N/A

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

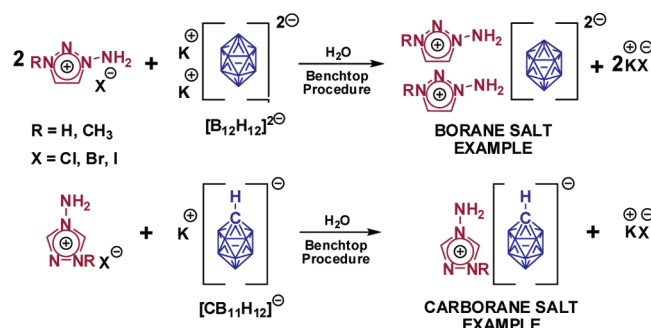
Scott A. Shackelford,^{*} John L. Belletire,[†] Jerry A. Boatz, Stefan Schneider, Amanda K. Wheaton,[†] Brett A. Wight,[†] Leslie M. Hudgens,[†] Herman L. Ammon,[‡] and Steven H. Strauss[§]

Air Force Research Laboratory, Propellants Branch (AFRL/RZSP), 10 East Saturn Boulevard, Edwards AFB, California 93524-7680, Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, and Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

scott.shackelford@edwards.af.mil

Received March 16, 2009

ABSTRACT



Ten new salts that pair triazolium and imidazolium cations with *closo*-icosahedral anions $[\text{B}_{12}\text{H}_{12}]^{2-}$ and $[\text{CB}_{11}\text{H}_{12}]^-$ were synthesized in water solvent using an open-air, benchtop method. These unreported [Heterocyclium]₂[B₁₂H₁₂] and [Heterocyclium][CB₁₁H₁₂] salts extend reports of [Imidazolium][CB₁₁H₁₂] and [Pyridinium][CB₁₁H₁₂] 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 $[\text{B}_{12}\text{H}_{12}]^{2-}$ 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 salt¹ followed by a subsequent report of nonhygroscopic, air stable, binary

[†] ERC, Inc. contractor at AFRL/RZSP, Edwards AFB.

[‡] University of Maryland, College Park, MD.

[§] Colorado State University, Ft. Collins, CO.

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

We now report the synthesis and characterization 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 stability⁶ 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 [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 [Triazolium] $[CB_{11}H_{12}]$ **6–9** and one new [Imidazolium] $[CB_{11}H_{12}]$ **10** salts also are described which extend properties characterization beyond several [Imidazolium] $[CB_{11}H_{12}]$ ⁹ and one [Pyridinium] $[CB_{11}H_{12}]$ ¹⁰ salts that previously were reported.

The former [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 heterocyclium 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 displays the five heterocyclinium borane salts synthesized by our benchtop, open-air, aqueous procedure.

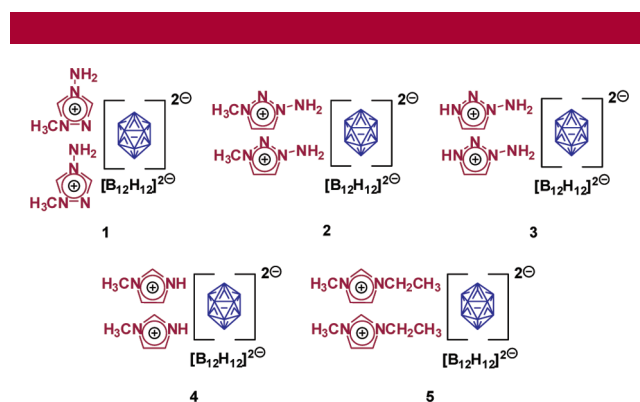


Figure 1. [Heterocyclium] $_2[B_{12}H_{12}]$ borane salts prepared.

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-methylimidazolium borane **5**, appear in the Supporting Information.

Figure 2 shows the six new [Heterocyclium] $[CB_{11}H_{12}]$ 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-

(1) Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, 21, 1263.

(2) Wilkes, J. S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, 965.

(3) Drake, G.; Hawkins, T.; Brand, A.; Hall, L.; McKay, M. *Propellants, Explos., Pyrotech.* **2003**, 28, 174.

(4) Shackelford, S. A. U.S. Patent 7 521 564, 2009.

(5) Pitochelli, A. R.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, 82, 3228.

(6) Kaszynski, P. *Collect. Czech. Chem. Commun.* **1999**, 64, 895, and references therein.

(7) (a) Grimes, R. N. *Angew. Chem., Int. Ed.* **2003**, 42, 1198, and references therein. (b) Muetterties, E. L.; Knoth, W. H. *Polyhedral Boranes*; M. Dekker: New York, 1969.

(8) Knoth, W. H. *J. Am. Chem. Soc.* **1967**, 89, 1274.

(9) Larsen, A. S.; Holbrey, J. D.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **2000**, 122, 7264.

(10) Zhu, Y.; Ching, C.; Carpenter, K.; Xu, R.; Selvaratnam, S.; Hosmane, N. S.; Maguire, J. A. *Appl. Organometal. Chem* **2003**, 17, 346.

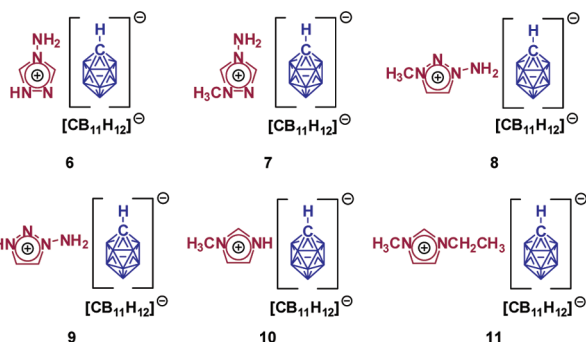


Figure 2. [Heterocyclium][CB₁₁H₁₂] carborane salts prepared.

cal.¹⁴ More detailed [Heterocyclium][CB₁₁H₁₂] salt syntheses for salts **6**–**11** appear in the Supporting Information.

Initial syntheses were conducted on a small 150–200 mg scale based on K₂[B₁₂H₁₂]²⁻ and K[CB₁₁H₁₂]. Once optimum conditions were determined for each salt, the metathesis reactions were conducted on a 1–4 g scale. The [B₁₂H₁₂]²⁻ salt of **3** was directly scaled from 2 to 5.5 g for K₂[B₁₁H₁₂] with a comparable yield and final purity.

(11) The K₂[B₁₂H₁₂]²⁻ and K[HCB₁₁H₁₁]⁻ reactants were purchased from Katchem Ltd., E. Krasnohorská 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][*closo*-B₁₂H₁₂]²⁻, **1**: Solid [4-Amino-1-methyl-1,2,4-triazolium] iodide (4.52 g; 20.00 mmol), CH₃I methylated plus recrystallization from methanol) and commercial K₂[*closo*-B₁₂H₁₂]²⁻ (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; (recrystallized portion = 87.6% recovery); overall purified yield = 79.7%); ¹H 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); ¹³C 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*-CB₁₁H₁₂]⁻, **9**: Solid [1-Amino-3-H-1,2,3-triazolium] chloride (2.41 g; 20.00 mmol) and commercial K[*closo*-CB₁₁H₁₂]⁻ (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[CB₁₁H₁₂]⁻ 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%); ¹H NMR 400 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 [CB₁₁H₁₂]⁻ *m/z* = 143.2035, found 143.2045.

The density, melting point, and reaction yields for salts **1** to **11** are listed in Tables 1–3. Experimental densities are

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

			melting point (°C) density (g/cc) pycnometry / 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

			melting point (°C) density (g/cc) pycnometry / 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.

obtained by pycnometry at rt and are compared to a newly developed predictive density additivity code¹⁵ 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

An X-ray crystal packing structure of [4-Amino-1-methyl-1,2,4-triazolium]₂[B₁₂H₁₂]²⁻ **1** appears in Figure 3. Single

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

(16) Preparing acceptable single crystals for X-ray analysis results in two occluded CH₃CN molecules for salt **2** and two occluded H₂O molecules for salt **3**. Both salts become amorphous powders when the solvent molecules are removed for pycnometry density analyses.

Table 3. Imidazolium Borane and Carborane Salts

$\left[\text{XN} \begin{array}{c} \diagup \diagdown \\ \text{C} \end{array} \text{NY} \right]^n$	$\left[\text{B}_{12}\text{H}_{12} \right]^{2-}$ n = 2	$\left[\text{CB}_{11}\text{H}_{12} \right]^-$ n = 1	melting point (°C)		yields (%)	
			density (g/cc)		direct ppt.	
			pycnometry / x-ray		(overall)	
			(predicted)			
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 ₂ CH 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 ₂ CH 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][B₁₂H₁₂] 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 previously reported [1-Ethyl-3-methylimidazolium]-[CB₁₁H₁₂] salt **11** was synthesized by a silver salt-based metathesis procedure.⁹ The earlier measured X-ray single crystal density of 1.07 g/cm³ compares well with our pycnometry density of 1.03 g/cm³, taken at rt, and the predicted density¹⁵ of 1.05 g/cm³ (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[B₁₂H₁₂] salt, analogous to [CB₁₁H₁₂][−] salt **6**, is absent from Table 1. Unique

(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.

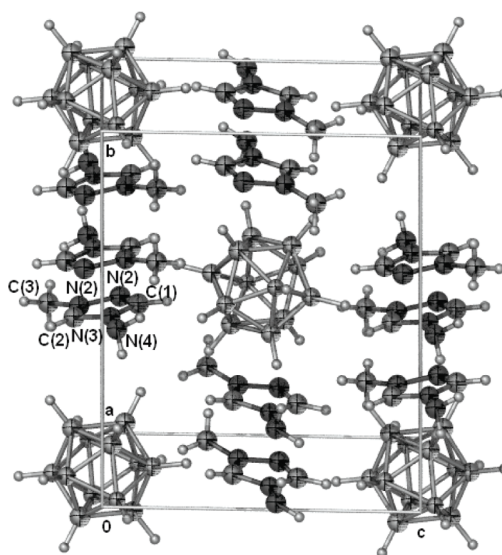


Figure 3. Crystal packing of salt **1** viewed along the crystallographic *a*-axis.

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 [B₁₂H₁₂]^{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][B₁₂H₁₂] using the heterocyclic cations seen in salts **1** and **11**.

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>.

OL900550V