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The Structure of Potassium and Tetramethylammonium Salts of the Cyclic Organohydroborate Anion $[H_2BC_8H_{14}]^-$ with Different Solvent Ligands

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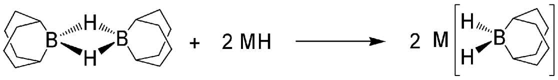
Solvated potassium salts of the 9-BBN hydroborate anion have been prepared and their structures have been determined by single-crystal X-ray diffraction analyses. A tetrameric complex $\{LK[(\mu\text{-}H)_2BC_8H_{14}]\}_4$ is formed when L is toluene, MeTHF, toluene/THF, THF/Et_2O mixtures. The basic framework consists of a distorted K_4B_4 cube in which potassium and boron are at alternate corners of the cube linked by bridging hydrogen atoms and α-C–H hydrogen atoms from the 9-BBN hydroborate that appear to form agostic interactions with potassium. There are two types of bridging hydrogen atoms: one is connected to three potassium atoms and one boron atom in a μ_4-coordination arrangement, and the other one is connected to two potassium atoms and one boron atom in a μ_3-coordination arrangement. There are four μ_4-hydrogen arrangements in the structure. They are located inside of the K_4B_4 cube. The four μ_3-hydrogen arrangements are located outside of the distorted K_4B_4 cube. The coordination number of potassium is 8 with the three μ_4-, two μ_3-bridging hydrogen atoms, two α-C–H hydrogen atoms, and one oxygen atom of the solvent, L (there is a weak π-η^6 interaction when the solvent is toluene). On the other hand, in the chelating solvent DME, a dimeric structure is formed in which the inner part is planar with potassium and boron located at alternate corners. The potassium is connected to four μ_3-bridging hydrogen atoms, two apparent agostic α-C–H bonding hydrogen atoms, and four oxygen atoms of two DME molecules. Its coordination number is 10 including the agostic interactions. The structure of the uncoordinated $[H_2BC_8H_{14}]^-$ anion is observed in the tetramethylammonium salt.

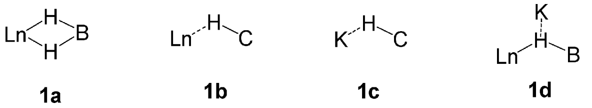
Introduction

Alkali metal (cyclooctane-1,5-diyl) dihydroborates (9-BBN hydriborate anion) have been readily prepared through the reaction of 9-borabicyclo[3.3.1]nonane dimer (9-BBN) with alkali metal hydrides in ether solvents[1] [reaction (1)]. These organohydroborates have been employed as chelating ligands through B–H–M bridges to produce a variety of complexes with transition metals,[2] lanthanides,[3,4] and actinides.[5]



(1)

In the divalent lanthanide complexes $[K(MeTHF)_3]_2\{Ln[(\mu\text{-}H)_2BC_8H_{14}]_4\}$ (MeTHF = 2-methyltetrahydrofuran, Ln = Eu, Yb),[3] four types of interaction between hydrogen and the metal atoms are reported (Scheme 1). The interactions **1a** and **1b** represent the commonly observed metal–hydrogen–boron bridge bond and metal-agostic hydrogen interactions observed in transition and lanthanide metal complexes of the 9-BBN hydroborate ion. The interactions **1c** and **1d** are observed in the complexes $[K(MeTHF)_3]_2\{Ln[(\mu\text{-}H)_2BC_8H_{14}]_4\}$.[3]



Scheme 1.

These observations provide the impetus to determine if interactions such as **1a**–**c**, and analogs of **1d** exist in the potassium salt of the anion $[(\mu\text{-}H)_2BC_8H_{14}]^-$. Thus investigation of the structure of the potassium salt of the 9-BBN hydroborate anion $[H_2BC_8H_{14}]^-$ was carried out. It was found that the structure of the potassium salt is a tetramer when crystallized as a toluene solvate. To compare the effect of solvate on the molecular character of $K[(\mu\text{-}H)_2BC_8H_{14}]$, crystals were also grown from MeTHF, DME, and mixed solvents. The structure of $[NMe_4][H_2BC_8H_{14}]$ was also determined since that of the uncoordinated 9-BBN hydroborate is apparently previously unreported.

Results and Discussion

1. Preparation

The solvate-free potassium salt of 9-BBN hydroborate was prepared by the literature method.[1] Samples were dis-

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Table 1. Crystallographic data for **1**, **2**, **3** and **4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{12}H_{28}BN$	$C_{60}H_{96}B_4K_4$	$C_{54}H_{96}B_4K_4O_2$	$C_{32}H_{72}B_2K_2O_8$
Formula weight (amu)	197.16	1017.01	976.95	684.72
Temperature [°C]	–73	–123	–73	–53
Crystal system	monoclinic	tetragonal	monoclinic	monoclinic
Space group	*C2/c*	I4(1)/a	*C2/c*	*C2*
a [Å]	19.6161(5)	22.918(5)	27.728(6)	15.798(1)
b [Å]	7.179(2)	22.918(5)	11.388(3)	18.848(1)
c [Å]	18.675(5)	11.410(3)	22.428(5)	15.592(1)
α [°]	90	90	90	90
β [°]	100.12(3)	90	126.22(3)	113.52(1)
γ [°]	90	90	90	90
V [Å^3]	2589.0(12)	5993(2)	5713(2)	4256.6(4)
Z	8	4	4	4
$D_{\text{calcd.}}$ [g cm^{-3}]	1.012	1.127	1.136	1.068
μ [mm^{-1}]	0.056	0.332	0.348	0.262
2θ range [°]	4.44–55.06	5.02–52.04	4.50–54.88	3.54–49.92
Index ranges	$-25 \le h \le 25$, $-9 \le k \le 9$, $-24 \le l \le 24$	$-28 \le h \le 28$, $-28 \le k \le 28$, $-13 \le l \le 14$	$-35 \le h \le 35$, $-14 \le k \le 14$, $-29 \le l \le 28$	$-18 \le h \le 18$, $-22 \le k \le 22$, $-18 \le l \le 18$
Reflections collected	11135	19051	12535	13963
Independent reflection	2978	2908	6507	7392
R_{int}	0.0274	0.0278	0.0222	0.0285
Completeness to θ [%]	99.7	98.6	99.6	99.8
Max/min transmission	0.9933,0.9894	0.9519,0.9040	0.9242,0.8879	0.9743,0.9422
Data/restraints/parameter	2978/0/239	2908/0/284	6507/0/395	7392/1/431
R_1 [$I > 2.0\sigma(I)$] [a]	0.0406	0.0369	0.0491	0.0523
wR_2 (all data) [b]	0.1098	0.0961	0.1398	0.1431
Goodness-of-fit on F^2	1.066	1.055	1.015	1.013
Largest difference peak and hole [e Å^{-3}]	0.244, –0.165	0.123, –0.185	0.416, –0.527	0.188, –0.182

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

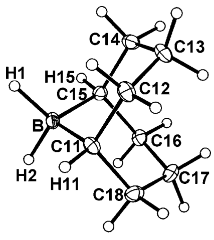
solved in the solvents toluene, 2-methyltetrahydrofuran (MeTHF), DME, a 1:1 mixture of toluene and THF, and a 1:1 mixture of THF and ether to form the corresponding solutions of the potassium salt. From these solutions, crystals suitable for X-ray diffraction analysis were obtained by slowly evaporating the solvent. The tetramethylammonium salt of 9-BBN hydroborate was prepared by a metathesis reaction between K[$H_2BC_8H_{14}$] and [NMe_4]Cl in THF and characterized by proton NMR, elemental analysis and single-crystal X-ray diffraction analyses. Crystal data are given in Table 1.

2. Structures

2.1 Structure of [NMe_4][$H_2BC_8H_{14}$] (1)

The reported lithium salts of 9-BBN hydroborates, [$(OEt_2)Li(H_2BC_8H_{14})]_2$, [$(THF)_2Li(H_2BC_8H_{14})]_2$, and [$(THF)_{0.5}(TMEDA)_{0.5}Li(H_2BC_8H_{14})]_2$ [DMEDA = $(CH_3)_2N(CH_2)_2N(CH_3)_2$] have been shown to be the dimers.[6] Interaction between alkali metal and the bridging hydrogen atoms and α-C–H hydrogen atoms occurs in these complexes. Sodium 9-BBN hydroborates, to the best of our knowledge, are unreported. Potassium 9-BBN hydroborates were reported earlier,[1] but without X-ray structures. In addtition to our earlier reported studies of the potassium 9-BBN hydroborate complexes of Yb and Eu,[3,4] we have examined and report here the structures of several potassium 9-BBN hydroborate solvates and that of the solvent free anion.

In order to obtain a structure of a simple 9-BBN anion not coordinated to a cation, the tetramethylammonium salt of 9-BBN hydroborate was prepared. The structure of the [NMe_4][$H_2BC_8H_{14}$] (**1**) is relatively simple, that of an ionic complex with separated [NMe_4]$^+$ cation and [$H_2BC_8H_{14}$]$^-$ anion. The structure of the anion is shown in Figure 1. This allows us to observe changes in the structure of the anion when it is coordinated to potassium in compounds **2**, **3** and **4** and a detailed discussion follows later. In the cation, average values are C–N 1.496(2) Å, C–H 0.97(2) Å, C–N–C 109.5(6)°, N–C–H 107.3(7)° and H–C–H 111.5(15)°.



1

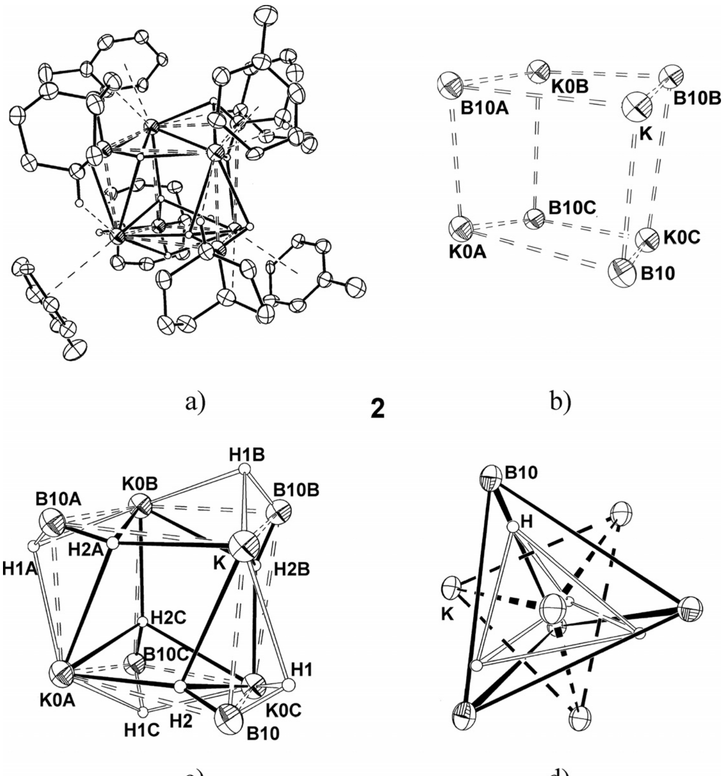
Figure 1. The structure of **1**, showing 25% probability thermal ellipsoids. Coordinates and isotropic temperature factors of all hydrogen atoms were allowed to vary and are drawn with arbitrary thermal ellipsoids.

2.2 Structure of {(Tol) K[(μ-H)$_2$BC$_8$H$_{14}$]}$_4$ (2)

The gross features of the structure of **2** (Figure 2, a) consist of a foundation that is a distorted K$_4$B$_4$ cube, with potassium and boron at alternate corners (Figure 2, b). The distances of K–B10, K–B10A, and K–B10B, three edges of the distorted cube, are 3.083(2), 3.749(2), and 3.033(2) Å. Angles B10–K–B10A, B10–K–B10B, and B10A–K–B10B are 92.7(1)°, 106.0(1)°, and 91.5(1)°, while the angles K–B10–K0A, K–B10–K0C, and K0A–B10–K0C are 85.7(1)°, 86.6(1)°, and 75.6(1)°. There are two types of bridging hydrogen atoms: four, four coordinate μ$_4$-H that reside in the cube and four three coordinate μ$_3$-H that are situated outside the cube (Figure 2, c). The unit may also be described as a cluster with its centroid at coordinates (0.5, 0.75, 0.625) and a fourfold axis of rotary-inversion along the crystal c-direction.

Potassium is also η^6-π coordinated to toluene and is involved in agostic interactions with two α-CH hydrogen atoms of the 9-BBN hydroborate ligands. The four μ$_3$ external bridging hydrogen atoms are located over four of the faces of the K$_4$B$_4$ cube and are close to being coplanar. In contrast, the four μ$_4$ bridging hydrogen atoms inside the cube are at the corners of a tetrahedron. This tetrahedron is inverted with and rotated approximately 60° with respect to the potassium tetrahedron, but maintains the same orientation as the boron tetrahedron (Figure 2, d). The potassium is bonded to three μ$_4$-H bridging hydrogen atoms and two μ$_3$-H bridging hydrogen atoms. The K–H distance with four-coordinate hydrogen atoms are 2.610(13), 2.750(13), and 2.917(13) Å, compared to those with three coordinate hydrogen atoms, 2.653(13) and 2.762(13) Å.

It is of interest that the cubic arrangement is also observed in the tetrameric sodium hydroborate complexes [(NaBMe$_3$H)$_4$OEt$_2$][7] and NaBH$_4$·TMTA (TMTA = trimethyltriazacyclononane).[8] But it is worth noting that in NaBH$_4$·TMTA, the BH$_4$ group supplies only one hydrogen atom for bridging to three Na centers, while the 9-BBN hydroborate ligand in complex **2** provides two bridging hydrogen atoms one of which is coordinated to three K atoms as μ$_4$-bridging hydrogen atoms and the other is coordinated



a) **2** b)

c) d)

Figure 2. a) The structure of **2**, showing 25% probability thermal ellipsoids. Bridging hydrogen atoms and α-hydrogen atoms are drawn with arbitrary thermal ellipsoids. All other hydrogen atoms omitted for clarity. b) The distorted K$_4$B$_4$ cube of the structure of **2**. Distances [Å]: K–B10 3.083(2); K–B10A 3.749(2); K–B10B, 3.033(2); angles [°]: B10–K–B10A 92.7(1), B10–K–B10B 106.0(1), B10A–K–B10B 91.5(1), K–B10–K0A 85.7(1), K–B10–K0C 86.6(1), K0A–B10–K0C 75.6(1). The twofold rotation axis along the *c*-direction relates K to K0A, K0B to K0C, B10 to B10A, B10B to B10C. The K atoms are calculated to be 2.67 Å from the centroid and the B atoms 3.01 Å. c) The interactions between the potassium and the μ$_4$- and μ$_3$-coordination bridging hydrogen atoms in the structure of **2**. Distances [Å]: K–H1 2.653(13), K–H1B 2.762(13), K–H2 2.917(13), K–H2A 2.610(13), K–H2B 2.750(13) and B10–H1 1.259(14), B10–H2 1.234(14). d) The relationship among the three tetrahedrons. Four μ$_4$-hydrogen atoms at distances [Å]: H2–H2A 2.99(2), H2–H2B 3.39(2), H2–H2C 3.39(2); angles [°]: H2–H2B–H2A 63.8(5), H2–H2C–H2A 63.8(5), H2–H2C–H2B 52.5(4); four potassium atoms at distances [Å]: K–K0A 4.673(2), K–K0B 4.196(2), K–K0C 4.196(2); angles [°]: K–K0C–K0A 56.2(1), K–K0B–K0A 56.2(1), K–K0C–K0B 67.7(1); four boron atoms at distances [Å]: B10B–B10A 4.964(2), B10–B10B 4.886(2), B10–B10C 4.886(2); angles [°]: B10–B10B–B10A 59.5(1), B10–B10C–B10A 59.5(1), B10–B10C–B10B 61.1(1).

to two K atoms as μ_3-bridging hydrogen atoms. The coordination geometries of the μ_4-bridging hydrogen atoms in complex **2** are very similar to those in the Na_4H_4 unit in the complexes $(NaBMe_3H)_4OEt_2$ and tetrameric $NaBH_4\cdot TMTA$.[7,8]

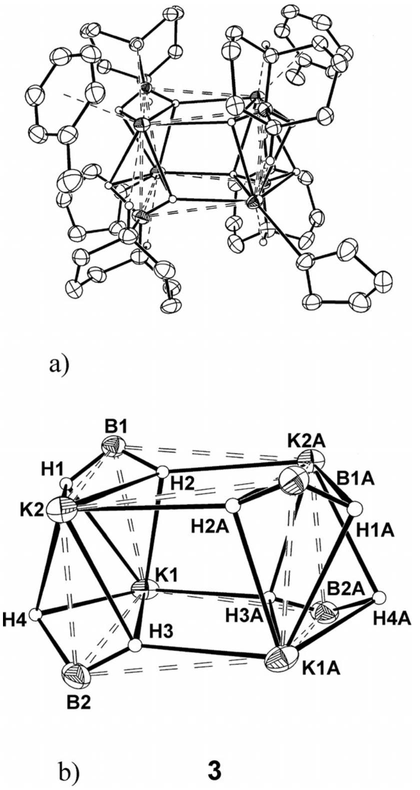
In complex **2**, the potassium also interacts with two α-C–H hydrogen atoms by apparent agostic interaction (Figure 2, a). These occur between the K atom and H11 and H15 with distances of K–H11, 2.716(16) and K–H15, 2.769(16) Å, which are comparable to the distances of potassium with bridging hydrogen atoms, K–H1 [2.653(14), 2.762(14) Å] and K–H2 [2.917(14), 2.610(14) Å, 2.750(14) Å].

In the molecular structure of complex **2** (Figure 2, a), the toluene molecule is disordered with fractional occupancies of 0.581(5) for part (A) and 0.419(5) for part (B). They interact in η^6-π coordination with potassium with the K–C distances ranging from 3.267(8) to 3.407(12) Å. Though long known experimentally and much studied theoretically, alkali metal-π (arene) interactions have recently taken on a new significance with the suggestion that intramolecular cationic interactions with (electron-rich) aromatic centers can influence protein structures.[9] Such interaction can best be described as an induced dipole interaction[10] with K–C distances for the η^6-bound toluene molecules in the range 3.267(8)–3.407(12) Å.[11,12] These distances are comparable to those found in the group of K-η^6-toluene in corresponding complexes. The interactions between K and η^6-toluene as well as with two α-C–H hydrogen atoms also contribute to the stabilization of the tetrameric species of **2** in addition to the potassium to BH contacts.

2.3 Structure of [(THF)$_2$(Tol)$_2$K$_4$]{H$_2$BC$_8$H$_{14}$}$_4$ (3)

The structure of **3** was obtained from a single crystal grown in a mixed solvent of THF and toluene in approximately 1:1 ratio (Figure 3, a). It is a tetrameric structure with two THF and two toluene ligands coordinated to four potassium atoms. [One of the 9-BBN ligands is disordered with occupancies for part B1 = 0.743(3) and 0.247(3) for part B3. Only the B1 anion is drawn in the figures.] The arrangement of 9-BBN hydroborate anions coordinated to potassium is different than that in structure **2**. The K_4B_4 cube is much more distorted. Though the μ_3- and μ_4-types of bridging hydrogen atoms exist in the structure of **3**, the geometrical arrangement differs from that in structure **2**. Four μ_4-bridging hydrogen atoms are still located inside of the K_4B_4 distorted cube, which is similar to that in structure **2**. However, four μ_3-bridging hydrogen atoms are associated with only two faces (Figure 3, b).

This arrangement differs from that of **2**, in which four μ_3-bridging hydrogen atoms are located at four faces (Figure 2, c). Thus the twelve K–B edges of the distorted K_4B_4 cube are divided into two types, four with an average length 3.702(4) Å and eight shorter ones with an average length of 3.020(4) Å. The centroid of this structure is at (0.5, 0.40699, 0.25) and it possesses a twofold axis parallel to the *b*-axis of the crystal (Figure 3, b) in a manner similar to that of structure **2**. The distances of potassium and bridging hydrogen atoms fall in the normal range with the longest 2.82(2) Å and the shortest 2.60(3) Å. In addition, potassium also appears to interact with two α-C–H hydrogen atoms by agostic interaction to complete its coordination sphere. The potassium α-C–H hydrogen distances: K1–H15 2.80(2), and K2–H11 2.75(2) Å are comparable to those in structure **2**.



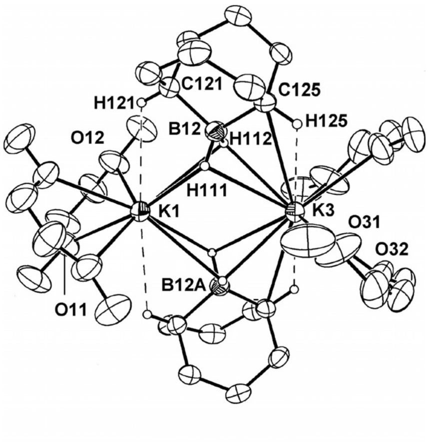
a)

b) **3**

Figure 3. a) The structure of **3**, showing 25% probability thermal ellipsoids. Bridging hydrogen atoms and α-hydrogen atoms are drawn with arbitrary thermal ellipsoids. All other hydrogen atoms omitted for clarity. b) The interactions between the potassium and μ_4- and μ_3-bridging hydrogen atoms in the structure of **3**. Distances [Å]: K1–B2A 3.636(4), K2–B1A 3.768(5), K1–B1 2.987(2), K1–B2 3.038(4), K2–B1 3.026(2), K2–B2 3.028(4), K1–H1 2.63(2), K1–H2 2.71(4), K1–H3 2.71(2), K1–H4 2.75(3), K2–H1 2.67(2), K2–H2 2.82(2), K2–H3 2.71(2), K2–H4 2.60(3); angles [°]: B1–K1–B2 97.29(8), B1–K1–B2A 103.3(1), B2–K1–B2A 96.1(1), B1–K2–B2 96.66(9), B1–K2–B1A 90.9(1), B2–K2–B1A 99.5(1), K1–B1–K2 82.63(6), K1–B1–K2A 77.7(1), K2–B1–K2A 87.5(1), K1–B2–K2 81.76(9), K1–B2–K1A 81.8(1), K2–B2–K1A 79.4(1).

2.4 Structure of [(DME) K(H$_2$BC$_8$H$_{14}$)]$_2$ (4)

The molecular structure of **4** is a dimer. In the asymmetric unit there are two half-molecular fragments that produce two similar molecules through symmetry operations. In one molecule a twofold axis passes through K1 and K3 and is perpendicular to B12–B12A. In the other a twofold axis passes through B1 and B2 and is perpendicular to K2–K2A. One molecule is displayed in Figure 4 in which K1, K3, B12, and B12A are shown. Distances B12–K1 and B12–K3 are 3.156(5) and 3.125(5) Å; angles K1–B12–K3, B12–K1–B12A, and B12–K3–B12A are 82.73(9), 96.6(2), and 97.9(2)°. The K1–K3 distance, 4.151(2) Å, is comparable to those in structure **2**. Each potassium atom is bound to four oxygen atoms from the DME ligands, four bridging hydrogen atoms, and two α-C–H hydrogen atoms by agostic interaction. All bridging hydrogen atoms are bound to one boron atom and two potassium atoms as μ_3-hydrogen atoms. The K1–H121 distance of 2.98(4) Å is comparable to 2.68(3) Å of the K1–H111, 2.91(4) Å of K1–H112, here the hydrogen atoms come from the K–H–B bridges. The K1–O11 and K1–O12 distances are 2.765(4) and 2.808(3) Å which are comparable to ordinary K–O bond lengths.[3] Thus the coordination number of K appears to be 10. Corresponding values for the second molecule present in the structure are given in the electronic supporting information.



4

Figure 4. The structure of **4**, showing 25% probability thermal ellipsoids. Bridging hydrogen and α-hydrogen atoms are drawn with arbitrary thermal ellipsoids. All other hydrogen atoms omitted for clarity. The interaction between the potassium and the four oxygen atoms from the two DME and six hydrogen atoms including the four μ_3-bridging hydrogen atoms, and the two α-C–H hydrogen atoms by agostic interaction. Distances [Å]: K1–O11 2.808(3), K1–O12 2.765(4), K1–H111 2.68(3), K1–H112 2.91(4), K1–H121 2.98(4).

Table 2 compares bond parameters of **1**, **2**, **3**, **4** and the 9-BBN dimer $(C_8H_{14}B)(\mu\text{-}H)_2(BC_8H_{14})$.[13] For the compounds bond parameters are not noticeably different with the exception of the B–H distance in **4** which is still within 2σ of the corresponding bond length in the other 9-BBN hydroborate ligands. That the $[H_2BC_8H_{14}]^-$ anion readily functions as a ligand in forming bridge bonds with potassium in the dimeric and tertrameric molecules can be related to the fact that these bond parameters are virtually unchanged in the formation of the dimeric and tetrameric complexes (see electronic supporting information for details). This also appears to be true for the dimeric 9-BBN hydroborate complexes of lithium.[6]

That with the solvent DME a dimer is formed rather than a tetramer is related to the fact that the DME is bidentate with its two oxygen atoms coordinating to potassium, thereby occupying an additional coordination site than the monodentate ether ligands thus blocking possible further association through a K–H–B bridge. Compared to the 9-BBN dimer, the obvious difference is that the angle of H–B–H, 87(2)°, is about 20° smaller than those in **1**, **2**, **3** and **4**.[14] This smaller HBH angle in the 9-BBN dimer and other diboranes probably relates to the significantly smaller size of boron compared to the alkali metals.[15]

Table 2. The comparison of bond parameters that involve the boron atom in complexes **1**, **2**, **3**, **4** and 9-BBN dimer {all data are average value and the standard deviations of the average values are calculated either by $[\Sigma(l_i - l)^2/n(n-1)]^{1/2}$ or $1/n(\Sigma\sigma_i^2)^{1/2}$, the larger value being reported}.

	Distances [Å]		Angles [°]		
	B–H	B–C	H–B–H	H–B–C	C–B–C
1 (ion pair)	1.195 (10)	1.626(3)	107.5(9)	111.2(4)	104.98(8)
2 (tetramer)	1.247 (12)	1.627(3)	108.7(9)	110.8(7)	104.89(13)
3 (tetramer)	1.16(2)	1.628(19)	106.6(22)	111.9(21)	103.9(9)
4 (dimer)	1.08(8)	1.629(9)	106(2)	112(1)	103.9(5)
9-BBN dimer	1.25(2)	1.567(2)	87(2)		111.8(3)

2.5 Structures of $[(MeTHF)\,K(H_2BC_8H_{14})]_4$ (5), $[(OEt_2)\,K(H_2BC_8H_{14})]_4$ (6a) and $[(THF)_2(OEt_2)_2K_4]\{H_2BC_8H_{14}\}_4$ (6b)

Poor quality crystals of **5** were grown from 2-methyltetrahydrofuran (MeTHF) and of **6** from mixtures of THF and diethyl ether (see chapter X-ray Structure Determination and the electronic supporting information for details). The structure of molecule **5** is similar to that of **2**. The K–K distances in **5** range from 4.050(6) to 4.506(6) Å. They are comparable to those in structure **2**. The formation of the tetramer is believed to be mainly dependent on the interaction between potassium and bridging hydrogen atoms. When the solvent is a monodentate ligand or a π donor the tetrameric structure is formed. The potassium is bound to one oxygen atom from 2-methyltetrahydrofuran (MeTHF) and seven hydrogen atoms including three μ_4-hydrogen atoms, two μ_3-hydrogen atoms, and two α-C–H hydrogen atoms by agostic interactions. The K–H distances range from 2.64(6) to 2.86(7) Å. They are not significantly different whether the hydrogen is from μ_4-hydrogen atoms or μ_3-hydrogen atoms, even from α-C–H hydrogen atoms by agostic interaction.

There are two independent molecules **6a** and **6b** in the unit cell for the structure of a single crystal obtained from the mixed solvent of ether and THF. The structure of **6a** contains four ether molecules, while the structure of **6b** contains two ether molecules and two THF molecules coordinated to potassium atoms, respectively. Both structures are tetramers and the inner part is the distorted K_4B_4 cube and the structural descriptions are similar to those of **2** and **3**.

Summary

The solid-state structure of an alkali metal 9-BBN hydroborate is dependent on the alkali metal size and other coordinating ligands. The 9-BBN hydroborate salts of lithium are dimeric structures with ether or THF ligands. The coordination number of lithium is 5 or 6 with bridging hydrogen atoms, α-C–H hydrogen atoms in agostic interactions, and oxygen atoms of ether or THF in the structure of those complexes.[6] However, the 9-BBN hydroborate salts of potassium, form tetrameric structures in the non-coordinating solvent toluene, the single dentate coordinating solvents MeTHF, THF, ether, and/or their 1:1 mixtures. The coordination number is 8 with three μ_4-, two μ_3-bridging hydrogen atoms, two α-C–H hydrogen atoms and one oxygen atom of solvent (or the weak η^6 interaction with the π system of toluene). The chelating ligand DME prevents formation of the tetramer of 9-BBN hydroborate salt instead the dimer, **4**, is formed in which the coordination number of potassium is 10 with four μ_3-bridging, two α-C–H hydrogen atoms and four oxygen atoms of the DME ligand.

The striking structural feature of the tetrameric structure of the potassium salts of 9-BBN hydroborate is that the K_4B_4 core is a much distorted cube. Similar arrangements occur in complexes $(NaBMe_3H)_4OEt_2$[7] and $NaBH_4$·TMTA,[8] which have only one bridging hydrogen. In contrast to a very distorted K_4B_4 cube in the potassium salts of 9-BBN hydroborate, a much more regular M_4O_4 cube is a typical structure for alkali metal alkoxides $[MOR]_4$.[16] In the systems studied, interaction between B–H hydrogen atoms and α-C–H hydrogen atoms with potassium is a question of interest. Evidences for such interactions have been given by single-crystal X-ray diffraction and infrared and NMR spectroscopy.[17] The spectra we obtained were too complicated to decipher with confidence. But low temperature single-crystal X-ray diffraction, is suggestive of such an interaction.

The tetramethylammonium salt of 9-BBN hydroborate provides the structure of the anion $[H_2BC_8H_{14}]^-$.

Experimental Section

General Comments: All manipulations were carried out on a standard high vacuum line or in a dry box under nitrogen. Toluene, 2-methyltetrahydrofuran, tetrahydrofuran, DME, and ether were dried with sodium/benzophenone and freshly distilled prior to use. Celite was dried by heating at 150 °C under dynamic vacuum for 5 h. Potassium hydride (Aldrich) was received as an oil slurry, washed with hexane, vacuum dried, and stored in the drybox. $C_8H_{14}B(\mu\text{-}H)_2BC_8H_{14}$, and NMe_4Cl were purchased from Aldrich and used as received. Solvent-free $K[H_2BC_8H_{14}]$ was prepared by literature procedures.[1] Elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, TN, U.S.A. NMR spectra were recorded with a Bruker AM-250 spectrometer. ^1H NMR spectra were obtained at 250.1 MHz, and referenced to residual solvent protons. ^{11}B NMR spectra were obtained at 80.3 MHz, and externally referenced to BF_3·OEt_2 in C_6D_6 (δ = 0.00 ppm). Infrared spectra were recorded with a Mattson–Polaris FT-IR spectrometer with 2 cm^{-1} resolution.

X-ray Structure Determination: Single-crystal X-ray diffraction data were collected with a Nonius Kappa CCD diffraction system, which employs graphite-monochromated Mo-K_α radiation (μ = 0.71073 Å). A single crystal of a complex, **1** to **6**, was mounted on the tip of a glass fiber coated with Fomblin oil (a pentafluoro polyether). Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using the DENZO-SMN package (Nonius BV, 1999).[18] The empirical absorption correction was applied with the SORTAV program[19] provided by *MaXus* software.[20] The positions of the heavy atom K were revealed by the Patterson method. The structures were refined using the SHELXTL-97 (difference electron density calculations and full-matrix least-squares refinements) structure solution package.[21] Data merging was performed using the data preparation program supplied by SHELXTL-97. Other calculations was made using WinGX (version 1.70.01), which includes Platon, Parst programs.[22] After all non-hydrogen atoms were located and refined anisotropically, hydrogen atom positions were calculated assuming standard geometries. All hydrogen atoms of both the organohydroborate ring and the tetramethylammonium group in **1**, all hydrogen atoms of the organohydroborate ring in **2**, and bridge hydrogen atoms and α-hydrogen atoms of the organohydroborate ring in **3** to **6** were located on difference maps and their positional and isotropic thermal parameters were refined. This is the commonly accepted procedure for locating hydrogen atoms by X-ray diffraction and distances are probably within a 0.1 Å if the atom bound to hydrogen is not a heavy fifth or sixth row element.

In **2** the toluene molecule is disordered [fractional occupancies 0.587(6), 0.413(6)] with average ring distances <C–C> 1.39(2) and 1.38(5) Å, respectively, and for the ordered 9-BBN group <C–C> 1.535(2) Å. In **3**, one 9-BBN group is ordered, <C–C> 1.534(2) Å. A second 9-BBN group is disordered [fractional occupancies 0.745(4) and 0.255(4)] with <C–C> 1.535(5), 1.53(1) Å, respectively. All agostic contacts have been calculated only with respect to the ordered 9-BBN group. In **4** there is no apparent disorder and for the three independent 9-BBN groups present <C–C> 1.523(5), 1.523(2), and 1.520(2) Å. The crystals grown for compounds **5** and **6** were of poor quality. Crystals of **5** were merohedrally twinned and disordered while many atoms in the THF and ether ligands of **6** were split and large difference electron density residuals remained after all atoms had been located. The data for these compounds has been relegated to the supporting information.

CCDC-620329 to -620334 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of $[NMe_4][H_2BC_8H_{14}]$ (1): $K[H_2BC_8H_{14}]$ (0.162 g, 1.0 mmol) and NMe_4Cl (0.110 g, 1.0 mmol) were put into a flask in the dry box. The flask was degassed and about 10 mL of THF was condensed into the flask. The system was warmed and stirred at room temperature for 3 h to produce **1** and a KCl precipitate. Then the mixture was filtered to remove the KCl solid. THF solution was concentrated at room temperature and colorless X-ray quality crystals 0.180 g (0.91 mmol, 91.3% yield) formed. ^{11}B NMR (250 MHz, [D$_8$]toluene, 25 °C, BF_3·OEt_2): δ = –15.0 (t) ppm. ^1H NMR (250 MHz, [D$_8$]toluene, 25 °C, TMS): δ = 2.36 (s, 12 H, Me), 2.27–0.658 (m, α-, β-, γ-H of $H_2BC_8H_{14}$ unit) ppm. $^1H\{^{11}B\}$ NMR (250 MHz, [D$_8$]toluene, 25 °C, TMS): δ = 1.34 (s, μ-H of $H_2BC_8H_{14}$ unit) ppm. IR (KBr): $\tilde{\nu}$ = 3108 (w), 3074 (m), 2975 (w), 2920 (sh), 2873 (vs), 2826 (s), 1960 (w), 1849 (s), 1828 (sh), 1794 (m), 1733 (w), 1699 (m), 1651 (m), 1557 (m), 1539 (m), 1425 (vs), 1401 (sh), 1341 (s), 1315 (sh, w), 1284 (m), 1261 (m), 1203 (m), 1168 (w), 1111 (m), 1067 (m), 1041 (m), 1014 (vs), 928 (m), 888 (m), 865 (w), 828 (sh), 805 (vs), 734 (m), 463 (m) cm^{-1}. $C_{12}H_{28}BN$ $\{[N(CH_3)_4](H_2BC_8H_{14})\}$ (197.17): C 73.09, H 14.31, N 6.09; found C 73.18, H 14.70, N 5.84.

Preparation of $\{(Tol)K[(\mu\text{-}H)_2BC_8H_{14}]\}_4$ (2): Solvent-free $K[H_2BC_8H_{14}]$ (0.2 g) was dissolved in toluene to produce a $K[H_2BC_8H_{14}]$ solution. After it was filtered, the solution was concentrated at room temperature to afford colorless X-ray quality crystal of complex **2**. ^{11}B NMR (250 MHz, [D$_8$]THF, 25 °C, $BF_3\cdot OEt_2$): δ = –15.5 (t) ppm. $^{11}B\{^1H\}$ NMR (250 MHz, [D$_8$]THF, 25 °C, $BF_3\cdot OEt_2$): δ = –15.5 (s) ppm. ^{1}H NMR (250 MHz, [D$_8$]-THF, 25 °C, TMS): δ = 7.13 (m, C_6H_5 of toluene), 2.30–0.89 (m, CH_3 of toluene and β-, γ-H of $H_2BC_8H_{14}$ unit), 0.62 (s, α-H of $H_2BC_8H_{14}$ unit) ppm. $^1H\{^{11}B\}$ NMR (250 MHz, [D$_8$]THF, 25 °C, TMS): δ = 0.80 (s, μ-H of $H_2BC_8H_{14}$ unit) ppm. ^{11}B NMR (250 MHz, [D$_8$]toluene, 25 °C, $BF_3\cdot OEt_2$): δ = –17.2 (t) ppm. $^{11}B\{^1H\}$ NMR (250 MHz, [D$_8$]toluene, 25 °C, $BF_3\cdot OEt_2$): δ = –17.2 (s) ppm. ^{1}H NMR (250 MHz, [D$_8$]toluene, 25 °C, TMS): δ = 2.34–0.88 (m, CH_3 of toluene and β-, γ-H of $H_2BC_8H_{14}$ unit), 0.32 (s, α-H of $H_2BC_8H_{14}$ unit) ppm. $^1H\{^{11}B\}$NMR (250 MHz, [D$_8$]toluene, 25 °C, TMS): δ = 0.18 (s, μ-H of $H_2BC_8H_{14}$ unit) ppm. IR (KBr): ṽ = 2979 (m), 2946 (s, sh), 2915 (vs), 2862 (vs), 2829 (vs), 2808 (vs,sh), 2680 (w), 2647 (w), 2614 (w), 2361 (w), 2320 (w), 2236 (w,sh), 2198 (m,sh), 2158 (s), 2125 (s), 2077 (s), 1977 (s,sh), 1957 (s), 1487 (m), 1455 (m), 1384 (w), 1229 (s), 1160 (m), 1076 (m), 1037 (w), 984 (w), 939 (w), 901 (w), 829 (w), 794 (w), 683 (w), 613 (w), 526 (w), 472 (w), 420 (m) cm^{-1}. $\{[K(C_7H_8)_{0.05}(H_2BC_8H_{14})]_4\}$: $C_{8.35}H_{16.4}B_1K_1$ (166.73): calcd. C 60.15, H 9.91; found C 59.96, H 9.59.

Preparation of $[(DME)K(H_2BC_8H_{14})]_2$ (4): Solvent-free $K[H_2BC_8H_{14}]$ (0.2 g) was dissolved in DME to produce a $K[H_2BC_8H_{14}]$ solution. After it was filtered, the solution was concentrated at room temperature to afford colorless X-ray quality crystal of complex **4**: ^{11}B NMR (250 MHz, [D$_8$]THF, 25 °C, $BF_3\cdot OEt_2$): δ = –16.2 (t) ppm. $^{11}B\{^1H\}$ NMR (250 MHz, [D$_8$]THF, 25 °C, $BF_3\cdot OEt_2$): δ = –16.2 (s) ppm. ^{1}H NMR (250 MHz, [D$_8$]-THF, 25 °C, TMS): δ = 3.44 (s, CH_2 of DME), 3.28 (s, CH_3 of DME), 1.80–1.45 (m, β-, γ-H of $H_2BC_8H_{14}$ unit), 0.60 (s, α-H of $H_2BC_8H_{14}$ unit) ppm. $^1H\{^{11}B\}$ NMR (250 MHz, [D$_8$]THF, 25 °C, TMS): δ = 0.78 (s, μ-H of $H_2BC_8H_{14}$ unit) ppm. ^{11}B NMR (250 MHz, [D$_8$]toluene, 25 °C, $BF_3\cdot OEt_2$): δ = –17.2 (t) ppm. $^{11}B\{^1H\}$ NMR (250 MHz, [D$_8$]toluene, 25 °C, $BF_3\cdot OEt_2$): δ = –17.2 (s) ppm. ^{1}H NMR (250 MHz, [D$_8$]toluene, 25 °C, TMS): δ = 3.07–3.02 (m, CH_2 and CH_3 of DME), 2.32–1.83 (m, β-, γ-H of $H_2BC_8H_{14}$ unit), 0.38 (s, α-H of $H_2BC_8H_{14}$ unit) ppm. $^1H\{^{11}B\}$ NMR (250 MHz, [D$_8$]toluene, 25 °C, TMS): δ = 0.27 (s, μ-H of $H_2BC_8H_{14}$ unit) ppm. IR (KBr): ṽ = 2979 (m), 2946 (s, sh), 2915 (vs), 2863 (vs), 2828 (vs), 2807 (vs,sh), 2679 (w), 2647 (w), 2614 (w), 2319 (w), 2236 (w,sh), 2198 (m,sh), 2158 (s), 2125 (s), 2079 (s), 2040 (s,sh), 1977 (s,sh), 1957 (s), 1485 (m), 1450 (m), 1385 (w), 1337 (w), 1229 (s), 1159 (m), 1076 (m), 1037 (w), 939 (w), 903 (w), 829 (w), 794 (w), 731 (w), 682 (w), 527 (w), 473 (w), 421 (m) cm^{-1}. $\{[K(H_2BC_8H_{14})]_2\}$: $C_8H_{16}B_1K_1$ (162.12): calcd. C 59.26, H 9.95; found C 58.81, H 10.07.

Crystals of **3**, **5**, and **6** were obtained employing the same method as for the preparation of **2** and **4** by using the corresponding solvent or a mixture of solvents. Provided here are their structures without chemical analysis because they have very similar structures with **2**.

Supporting Information (see also the footnote on the first page of this article): Details of structural information for complexes **1**–**6** include crystallographic data and figures for **5** and **6**, BBN unit disorder in **3**, coordination environment of potassium in **4**, and the comparison of distances and angles of BBN in the coordinated arrangement in **2** and the non-coordinated arrangement in **1** are presented.

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