Synthesis and Crystal Structure of $(C_4H_8O\cdot Na^+)_2[2,3-(SiMe_3)_2-2,3-C_2B_4H_5^-]_2$: the First Ion Cluster of the *nido*-Carbaborane Cage Systems

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The ion cluster $(C_4H_8O\cdot Na^+)_2[2,3-(SiMe_3)_2-2,3-C_2B_4H_5^-]_2$, (2), has been prepared and the structure determined to show its extended network in the crystal lattice.

The synthesis of the monoanion of 2,3-dicarba-*nido*-hexaborane (8) was reported by Onak and Dunks nearly 22 years ago.[1] The solid-state structure of this anion has not been reported to date. Although the synthesis of the first dianion, $Na^+Li^+[2,3-(SiMe_3)_2-2,3-C_2B_4H_4]^{2-}$ was reported in 1986,[2] its solid-state molecular geometry is still unknown. Curiously, unlike the *nido*-C_2B_9 carbaborane derivatives[3] the disodium salts of the *nido*-C_2B_4 carbaboranes cannot be formed even by using excess of NaH in either polar or nonpolar solvents and at elevated temperatures.[1] In order to compare the solution geometry and the reactivity of the monoanion with those of the dianion, the *nido*-carbaborane precursor 2,3-(SiMe$_3$)$_2$-2,3-C$_2$B$_4$H$_6$ (1)[4] was allowed to react with a large excess of pure NaH in tetrahydrofuran (THF)† in a method identical to that employed by Onak and Dunks.[1] As the nature of the white

solid produced in this reaction could not be elucidated fully from spectroscopy‡ alone, this extremely air-sensitive solid was crystallized from benzene and an X-ray analysis was

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† Compound (1) (4.32 mmol) in THF (15 ml) was treated with NaH (10.41 mmol) *in vacuo* in a procedure identical to that described elsewhere[1] to isolate the title compound (2) as an extremely air-sensitive white solid in 92% yield (1.99 mmol). Compound (2) was crystallized in dry benzene for the X-ray analysis.

‡ *Spectroscopic and microanalytical data* for (2), $C_{24}H_{62}B_8O_2Na_2Si_4$. I.r. ($C_6H_6$ *vs.* C_6H_6): 3098 (s, s), 3080 (m, s), 3020 (w, s), 2950 (s, s), 2900 (sh), 2840 (sh) [ν(C–H)], 2536 (vs), 2464 (vs) [ν(B–H)], 1820 (m) [B–H–B(bridge)], 1480 (m), 1410 (sh) [δ(CH) asym], 1348 (w, s), 1320 (w, br) 1280 (s) [δ(CH) sym], 1150 (w, br.) 990 (s, br.), 831 (vvs, br.) [ρ(CH)], 755 (m, s), 680 (s, br.), 620 (m, s) [ν(Si–C)], 480 (vw, s), 418 (m, s), 389 (m, s) cm^{-1}. F.t. n.m.r. data: ^{1}H n.m.r.: (C_6D_6, relative to external Me$_4$Si) δ 4.05 [vbr.q, 2H, basal H$_t$, ^1J (^{1}H–^{11}B) ≈ 140 Hz], 3.52 (br.s, 4H, THF), 3.17 [vbr.q, 1H, basal H$_t$, ^1J(^{1}H–^{11}B) ≈ 138 Hz], 1.44 (br. s, 4H, THF), 0.52 (s, 18H, Me$_3$Si), −0.69 [br.q, 1H, apical H$_t$, ^1J(^{1}H–^{11}B) 173 Hz], −4.37 (br.s, 1H, bridge H); ^{11}B n.m.r. (C_6D_6, relative to external BF$_3$·OEt$_2$) δ 14.08 [vbr.d, 2B, basal BH, ^1J(^{11}B–^{1}H) ≈ 141 Hz], −3.78 [vbr.d, 1B, basal BH, ^1J(^{11}B–^{1}H) ≈ 140 Hz], −50.76 [d, 1B, apical BH, ^1J(^{11}B–^{1}H) 175 Hz]; ^{13}C n.m.r. (C_6D_6, relative to external Me$_4$Si) δ 113.60 (br.s, cage), 68.03 [t, THF, ^1J(^{13}C–^{1}H) 145.82 Hz], 25.43 [t, THF, ^1J (^{13}C–^{1}H) 132.80 Hz], 1.99 [q, Me$_3$Si, ^1J(^{13}C–^{1}H) 118.64 Hz]. Satisfactory elemental analyses were obtained (C, H, B, Si).
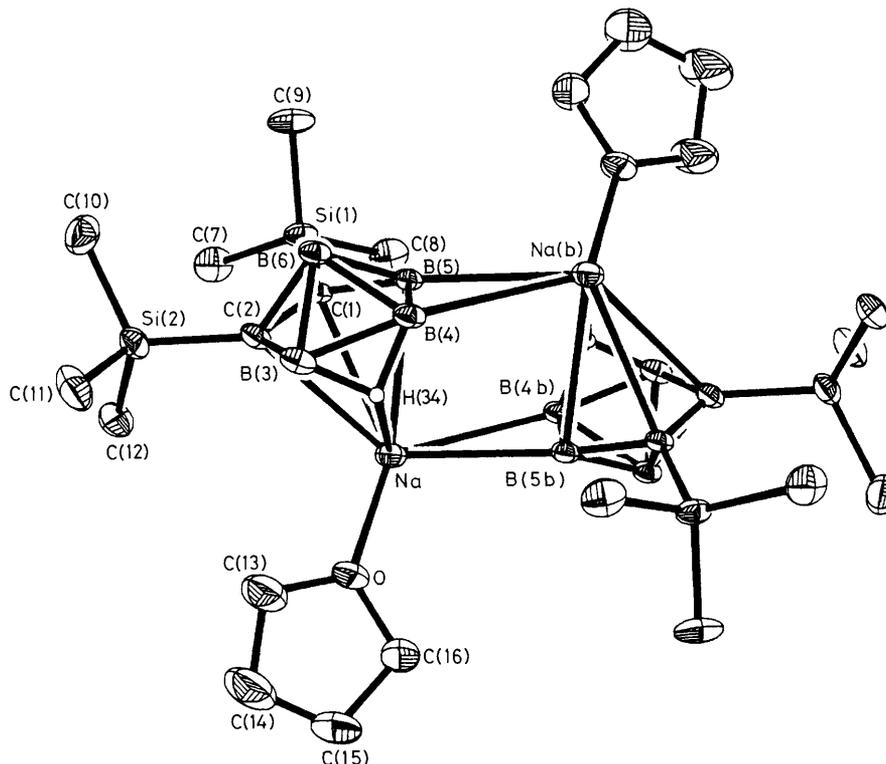
Figure 1. Structure of (2) showing the atom numbering scheme and thermal ellipsoids at the 30% probability level. An inversion centre lies half-way between the sodium ions. Pertinent parameters include Na–C(1) 2.832(10), Na–C(2) 3.071 (11), Na–B(3) 3.307 (11), Na–B(4) 3.290 (10), Na–B(5) 2.920 (11), Na–B(4b) 2.995 (12), Na–B(5b) 2.800 (11), Na–H(34) 2.57 (8), and Na–O 2.346 (9) Å.

done.§ This species was found to be the novel THF-solvated ion cluster, $(C_4H_8O \cdot Na^+)_2[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5^-]_2$, (2) (Figure 1).

The crystal packing diagram (Figure 2) is of an extended network of dimeric $\{Na^+[(SiMe_3)_2C_2B_4H_5]^-\}_2$ ion clusters that are layered almost symmetrically on top of each other. Each cluster consists of two C_2B_4 carbaborane cages and two THF-solvated sodium ions with a crystallographic inversion
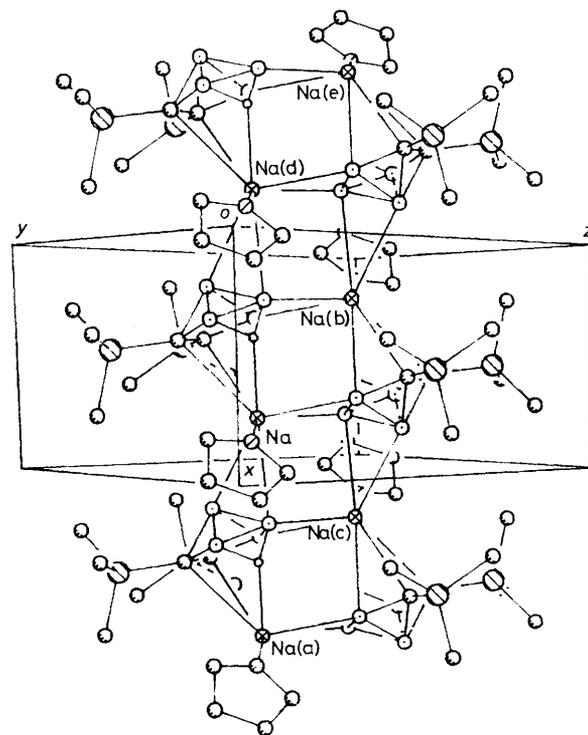
Figure 2. The crystal packing diagram showing the extended chain network of $\{Na^+[(SiMe_3)_2C_2B_4H_5]^-\}_2$ ion clusters.
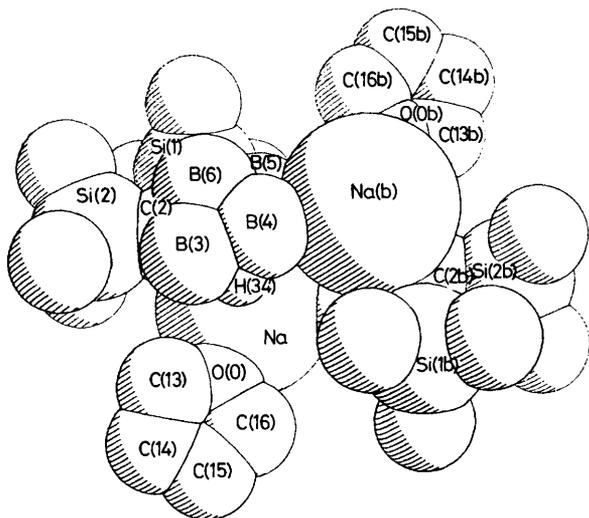
Figure 3. Space-filling model of (2).

centre half way between the sodium ions. Each Na⁺ is primarily involved in equal *exo*-polyhedral η^1-type bonding interactions with one of the basal borons in one cage [Na–B(5b) 2.800(11) Å] and the C(1) atom of the other cage [Na–C(1) 2.832(10) Å] (see Figure 1). While the interactions with the other cage atoms are weaker [Na–C(2) 3.071(11), Na–B(3) 3.307(11), Na–B(4) 3.290(10), Na–B(5) 2.920(11), Na–B(4b) 2.995(12), and Na–O 2.346(9) Å], the distance between Na and the bridged hydrogen [H(34)] is 2.57(8) Å. There is also a strong interaction between the sodiums in one [Na⁺(R₂C₂B₄H₅)⁻]₂ cluster and the apical and unique borons in a neighbouring cluster. For example, the Na–B$_{unique}$ and Na–B$_{apical}$ distances between the ion cluster units are 3.059(12) and 3.179(12) Å, respectively (see Figure 2). All sodium nearest neighbour distances are greater than that expected for covalent bonding and indicate that the interactions are all essentially ionic. It is clear from Figure 1, and even more apparent when a space-filling model is used (see Figure

3), that the second bridge hydrogens are very well protected within the cluster. Direct experimental studies on the relative acidities of *nido*-C₂B₄H₈ and *nido*-C₂B₉H₁₃, and their monoanions, are not available. However, AM1-SCF MO calculations[5] show that C₂B₉H₁₃ and C₂B₉H₁₂⁻ are more acidic than the C₂B₄-carbaborane analogues. However, if this structural arrangement of the monoanion cluster exists in solution as well, then it is possible that the failure of the second deprotonation by NaH could be a combination of (i) the less acidic nature of the second B–H–B bridge hydrogen, (ii) the protection of this hydrogen within the cluster, and (iii) the heterogeneous nature of the reaction between NaH and *nido*-carbaborane. A detailed study of these factors in the formation of various anions of the C₂B₄ carbaborane system is being carried out.

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