

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 derivatives³ 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-(SiMe₃)₂-2,3- $C_2B_4H_6$ (**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

[‡] 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) [$\nu(C-H)$], 2536 (vs), 2464 (vs) [$\nu(B-H)$], 1820 (m) [B-H-B(bridge)], 1480 (m), 1410 (sh) [$\delta(CH)$ asym], 1348 (w, s), 1320 (w, br) 1280 (s) [$\delta(CH)$ sym], 1150 (w, br.) 990 (s, br.), 831 (vvs, br.) [$\rho(CH)$], 755 (m, s), 680 (s, br.), 620 (m, s) [$\nu(Si-C)$], 480 (vw, s), 418 (m, s), 389 (m, s) cm^{-1} . F.t. n.m.r. data: ¹H n.m.r.: (C_6D_6 , relative to external Me₄Si) δ 4.05 [vbr.q, 2H, basal H_t, ¹J(¹H-¹¹B) \approx 140 Hz], 3.52 (br.s, 4H, THF), 3.17 [vbr.q, 1H, basal H_t, ¹J(¹H-¹¹B) \approx 138 Hz], 1.44 (br. s, 4H, THF), 0.52 (s, 18H, Me₃Si), -0.69 [br.q, 1H, apical H_t, ¹J(¹H-¹¹B) 173 Hz], -4.37 (br.s, 1H, bridge H); ¹¹B n.m.r. (C_6D_6 , relative to external BF₃·OEt₂) δ 14.08 [vbr.d, 2B, basal BH, ¹J(¹¹B-¹H) \approx 141 Hz], -3.78 [vbr.d, 1B, basal BH, ¹J(¹¹B-¹H) \approx 140 Hz], -50.76 [d, 1B, apical BH, ¹J(¹¹B-¹H) 175 Hz]; ¹³C n.m.r. (C_6D_6 , relative to external Me₄Si) δ 113.60 (br.s, cage), 68.03 [t, THF, ¹J(¹³C-¹H) 145.82 Hz], 25.43 [t, THF, ¹J(¹³C-¹H) 132.80 Hz], 1.99 [q, Me₃Si, ¹J(¹³C-¹H) 118.64 Hz]. Satisfactory elemental analyses were obtained (C, H, B, Si).

[†] 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 elsewhere¹ 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.

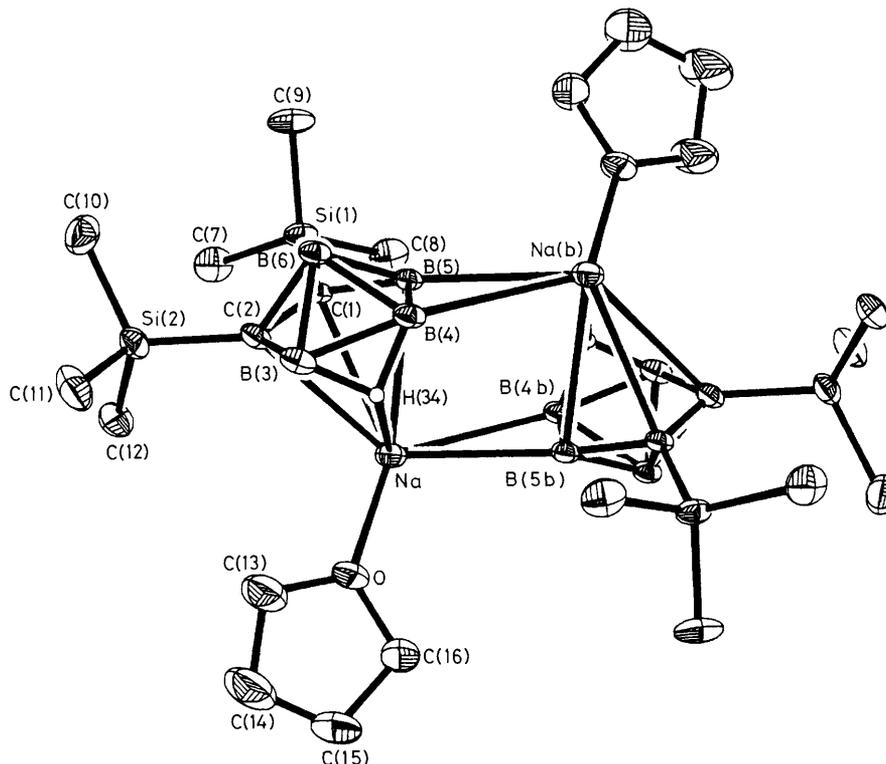


Figure 1. Structure of (2) showing the atom numbering scheme and thermal ellipsoids at the 30% probability level. An inversion centre lies half-way between the sodium ions. Pertinent parameters include Na–C(1) 2.832(10), Na–C(2) 3.071 (11), Na–B(3) 3.307 (11), Na–B(4) 3.290 (10), Na–B(5) 2.920 (11), 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, $(C_4H_8O \cdot Na^+)_2[2,3-(SiMe_3)_2-2,3-C_2B_4H_5^-]_2$, (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

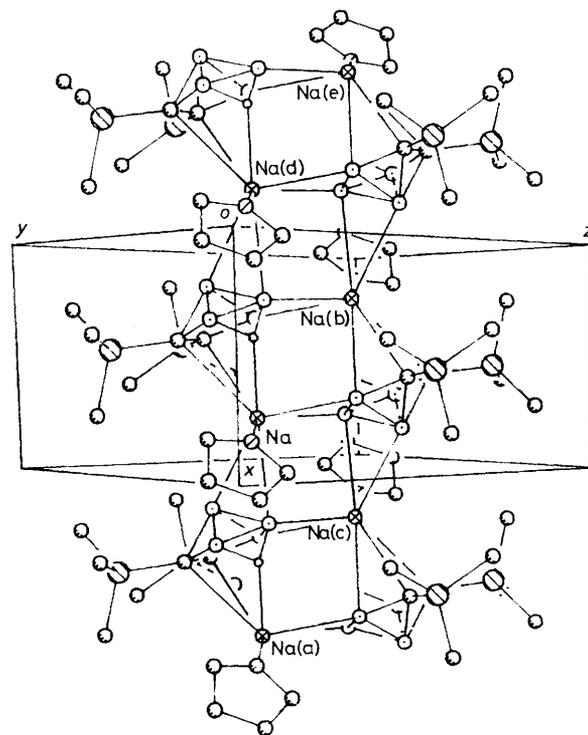


Figure 2. The crystal packing diagram showing the extended chain network of $\{Na^+[(SiMe_3)_2C_2B_4H_5^-]_2\}$ ion clusters.

§ *Crystal data* for (2), $C_{24}H_{62}B_8O_2Na_2Si_4$: $M = 627.68$, $a = 6.326(17)$, $b = 11.82(4)$, $c = 14.16(5)$ Å, $\alpha = 75.47(25)$, $\beta = 80.58(23)$, $\gamma = 80.50(22)^\circ$, $U = 1003(5)$ Å³, triclinic, space group $P\bar{1}$, $Z = 1$, and $D_c = 1.04$ g cm⁻³, $\mu(Mo-K\alpha) = 1.84$ cm⁻¹. Since the crystals were extremely air sensitive and changed to white amorphous solid upon removal of benzene *in vacuo*, they were sealed in 0.5 mm capillary tubes under an atmosphere of dry benzene. A total of 2636 reflections were collected at 213 K, on a Nicolet R3m/V diffractometer to $2\theta = 45^\circ$. Data were corrected for decay (~7%), Lorentz-polarization effects and for absorption. Structure was solved by direct methods programs used in SHELXTL-Plus (G. M. Sheldrick, 'Structure Determination Software Programs,' Nicolet Instrument Corp., U.S.A., 1988) and subsequent difference Fourier methods (SHELXTL-Plus system of programs automatically applies a factor which takes into account the size of the e.s.d.'s). Final full matrix least squares refinement (SHELXTL-Plus) using 2155 observed reflections with $I > 3.0\sigma(I)$ converged to $R = 0.086$ and $R_w = 0.092$. All nonhydrogen atoms were refined anisotropically. Cage hydrogen atoms H(34), H(3), and H(5) were located, the positions of H(4) and H(6) were calculated, and all were refined with fixed isotropic thermal parameters. The trimethylsilyl and THF ring H atoms were calculated and were constrained tetrahedrally. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

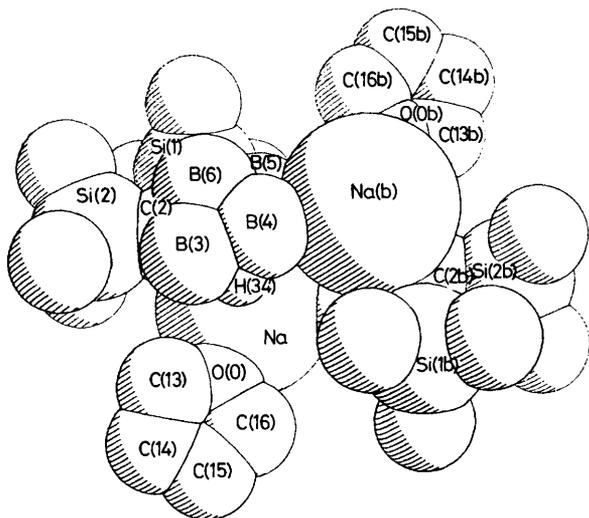


Figure 3. Space-filling model of (2).

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 [$\text{Na}-\text{B}(5\text{b})$ 2.800(11) Å] and the C(1) atom of the other cage [$\text{Na}-\text{C}(1)$ 2.832(10) Å] (see Figure 1). While the interactions with the other cage atoms are weaker [$\text{Na}-\text{C}(2)$ 3.071(11), $\text{Na}-\text{B}(3)$ 3.307(11), $\text{Na}-\text{B}(4)$ 3.290(10), $\text{Na}-\text{B}(5)$ 2.920(11), $\text{Na}-\text{B}(4\text{b})$ 2.995(12), and $\text{Na}-\text{O}$ 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 [$\text{Na}^+(\text{R}_2\text{C}_2\text{B}_4\text{H}_5)^-$]₂ cluster and the apical and unique borons in a neighbouring cluster. For example, the $\text{Na}-\text{B}_{\text{unique}}$ and $\text{Na}-\text{B}_{\text{apical}}$ 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*- $\text{C}_2\text{B}_4\text{H}_8$ and *nido*- $\text{C}_2\text{B}_9\text{H}_{13}$, and their monoanions, are not available. However, AM1-SCF MO calculations⁵ show that $\text{C}_2\text{B}_9\text{H}_{13}$ and $\text{C}_2\text{B}_9\text{H}_{12}^-$ are more acidic than the C_2B_4 -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 C_2B_4 carbaborane system is being carried out.

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References

- 1 T. Onak and G. B. Dunks, *Inorg. Chem.*, 1966, **5**, 439.
- 2 (a) N. S. Hosmane, P. de Meester, U. Siriwardane, M. S. Islam, and S. S. C. Chu, *J. Chem. Soc., Chem. Commun.*, 1986, 1421; (b) N. S. Hosmane and J. A. Maguire, in 'Advances in Boron and the Boranes,' vol. 5 in the series 'Molecular Structure and Energetics,' eds. A. Greenberg, J. F. Liebman, and R. E. Williams, VCH, New York, 1988, ch. 14, p. 297 and references cited therein; (c) N. S. Hosmane and J. A. Maguire, *Adv. Organomet. Chem.*, 1989, **30**.
- 3 (a) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, 1965, **87**, 1818; (b) M. F. Hawthorne and P. A. Wegner, *J. Am. Chem. Soc.*, 1965, **87**, 4392; (c) L. I. Zakharkin, E. I. Kukulina, and L. S. Podvisotskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 1866; (d) M. A. Grassberger, E. G. Hoffmann, G. Schomburg, and R. Köster, *J. Am. Chem. Soc.*, 1968, **90**, 56; (e) J. S. Roscoe, S. Kongpricha, and S. Papetti, *Inorg. Chem.*, 1970, **9**, 1561.
- 4 N. S. Hosmane, N. N. Sirmokadam, and M. N. Mollenhauer, *J. Organomet. Chem.*, 1985, **279**, 359.
- 5 J. A. Maguire and N. S. Hosmane, to be published.