Four-co-ordinate Hydrogen in the Cubane Structure of the Mono-etherate of the Sodium Hydridotriethylboronate Tetramer

By NORMAN A. BELL,*† (the late) HARRISON M. M. SHEARER, and CHRISTOPHER B. SPENCER
(*Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham* DH1 3LE)

Summary The crystal structure of the title compound consists of alternating sodium and hydrogen atoms at the corners of a very distorted cube, with one of the sodium atoms co-ordinated to an ether molecule and all the hydridic hydrogens bonded to the boron of a BMe_3 group.

HYDRIDES of the type MBR_3H (M = alkali metal, R = alkyl) are readily prepared from MH and R_3B[1–3] and some are now commercially available [R = Et, M = Li[4] (Superhydride): R = Bu[8], M = Li,[5] K[6] (L- and K-Selectride, respectively]. These highly attractive reducing agents for organic synthesis are capable of achieving stereo- and regio-selective transformations,[7] unequalled by any other reagent currently available. However, little is known about the nature of such reagents which have probably been assumed to contain the pseudo-tetrahedral hydridotrialkylboronate anion.

Sodium hydridotrimethylboronate obtained as described earlier from NaH and Me_3B[2] was recrystallised from hexane solution and dried in high vacuum, and is tetrameric in benzene solution.[8] Crystalline needles chosen for the *X*-ray study from the hexane solution were subsequently found to contain one mole of ether per tetramer.

Crystal data: monoclinic, space group‡ $P2_1/m$, lattice parameters (−140 °C) $a = 10{\cdot}046(4)$, $b = 10{\cdot}81(3)$, $c = 12{\cdot}842(6)$ Å, $\beta = 99{\cdot}54(2)°$, $Z = 2$ units of $(NaHBMe_3)_4OEt_2$. The structure was solved from visually estimated low temperature (−140 °C) equi-inclination Weissenberg data. Full-matrix refinement of the atomic co-ordinates derived from Patterson and Fourier methods with anisotropic temperature factors for all non-hydrogen atoms except the ether atoms, isotropic factors for all atoms of the ether molecule and the hydride hydrogens but not refining the

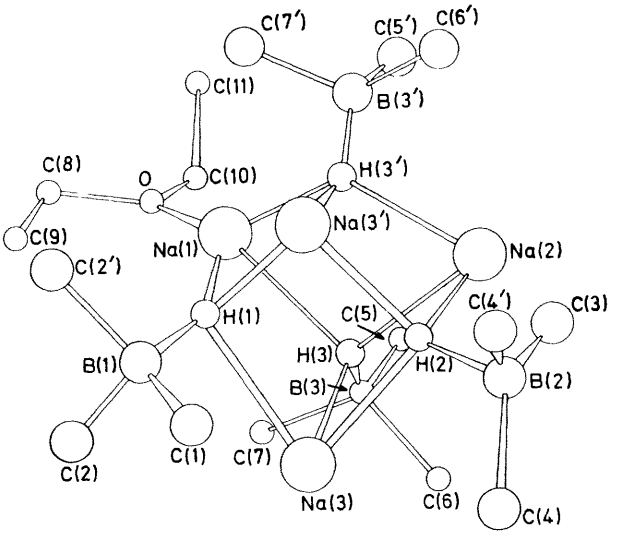

FIGURE. Structure of $(NaBMe_3H)_4OEt_2$; alkyl hydrogen atoms are omitted for clarity. Only one of the alternative positions for the ether molecule is shown.

† *Present address:* Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB.

‡ While systematic absences do not distinguish between space groups $P2_1/m$ and $P2_1$, subsequent analysis proved to be more satisfactory in $P2_1/m$ with the ether molecules disordered but close to the mirror plane.

positions of the remaining hydrogens has converged the conventional R factor to 0·105 for the 1252 reflections classified as observed §

The molecule has a cubane-type arrangement of sodium atoms and hydridic hydrogen atoms at alternate corners of a very distorted cube Atoms Na(1) and Na(2) lie on the mirror plane at $y = \frac{1}{4}$ with Na(3) below this plane and a related atom above it Similarly, B(1), B(2), H(1), H(2), C(1), and C(3) lie on this plane The ether atoms are close to this plane, especially the oxygen atom Each hydridic hydrogen is bonded to the boron of one BMe_3 group This arrangement means that the hydrogen atoms are 4-co-ordinate and three of the sodium atoms in the tetrameric unit are 3-co-ordinate while Na(1) is 4-co-ordinate by virtue of the co-ordination of the ether molecule The four sodium atoms lie at the corners of a tetrahedron and are much further apart (3·545—3·787 Å) than are the hydridic hydrogen atoms (2·611—2 802 Å) in their interpenetrating tetrahedron The four boron atoms lie at the corners of a much larger tetrahedron The twelve Na–H distances are not significantly different and lie in the range 2·25 to 2·42 Å The longest B–H linkage is that between B(2) and H(2) which is the only hydridic hydrogen not attached to Na(1) which is co-ordinated to an ether molecule The twelve Na–H–Na angles range from 100·5 to 114·2° while the H–Na–H angles are the same within experimental error with a mean of 71 9° The boron atoms are essentially tetrahedral, angles ranging from 106·0 to 113·5° (mean 109·4°) There are no significant differences in angles around the sodium atoms which are three- and four-co-ordinate

There are some very short intramolecular distances (2·28—2 36 Å) between sodium atoms and hydrogen atoms of methyl groups attached to boron as well as some weaker intermolecular interactions (2·56—2·73 Å) between tetramer units, involving Na(3) and Na(3′) with alkyl groups of neighbouring tetramers, similar to those found in $LiBMe_4$[9] and tetrameric methyl-lithium [10]

(*Received*, 14*th April* 1980, *Com.* 386)

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW Any request should be accompanied by the full literature citation for this communication

[1] H C Brown, A Khuri, and S C Kim, *Inorg Chem*, 1977, **16**, 2229
[2] P Binger, G Benedikt, G W Rotermund, and R Koster, *Justus Liebig's Ann Chem*, 1968, **717**, 21
[3] J B Honeycutt and J M Riddle, *J Am Chem Soc* 1961, **83**, 369, H C Brown, S Krishnamurthy, and J L Hubbard, *ibid*, 1978, **100**, 3343, H C Brown A Khuri and S Krishnamurthy, *ibid*, 1977, **99**, 6237 C A Brown and S Krishnamurthy, *J Organomet Chem*, 1978, **156**, 111, H C Brown, J L Hubbard, and B Singaram, *J Org Chem*, 1979, **44**, 5004
[4] H C Brown and S Krishnamurthy, *J Am Chem Soc*, 1973, **95**, 1669
[5] H C Brown and S Krishnamurthy, *J Am Chem Soc*, 1972, **94**, 7159
[6] C A Brown, *J Am Chem Soc*, 1973, **95**, 4100
[7] E R H Walker, *Chem Soc Rev*, 1976, **5**, 23
[8] N A Bell, G E Coates, and J A Heslop, unpublished observations
[9] W E Rhine, G Stucky, and S W Peterson, *J Am Chem Soc*, 1975, **97**, 6401
[10] E Weiss and R Wolfrum, *J Organomet Chem*, 1968, **12**, 257