

Some tetrahydroborate derivatives of aluminium: crystal structures of dimethylaluminium tetrahydroborate and the α and β phases of aluminium tris(tetrahydroborate) at low temperature

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The structures of several aluminium tetrahydroborates have been investigated, primarily by X-ray diffraction of single crystals at low temperatures. The structure of dimethylaluminium tetrahydroborate has been shown to consist of helical polymeric chains in which Me₂Al and BH₄ units alternate. The BH₄ groups exhibit bidentate ligation with respect to each of the adjacent metal atoms in a manner reminiscent of [MeZnBH₄] and Be(BH₄)₂. Solid aluminium tris(tetrahydroborate) exists in two phases with a transition temperature in the range 180–195 K. Each phase is made up of discrete Al(BH₄)₃ units in which the angle between AlB₂ and Al(μ -H)₂B planes is close to 90° and which conform within the limits of experimental error to *D*_{3h} symmetry; in the α phase these molecular units are disposed around a 2₁ crystallographic screw axis.

The isoelectronic nature of pairs of borane and hydrocarbon ligands (*e.g.* BH₄⁻ and CH₃⁻, B₃H₇ and C₃H₅⁺, B₅H₁₀⁻ and C₅H₅⁻) has been responsible for generating much interest in the structure and reactivity of metal hydroborate derivatives^{1–6} which may serve as paradigms for analogous hydrocarbon species. Thus, formation of the compounds [(η^5 -C₅Me₅)TaX]₂(B₂H₆) and [(η^5 -C₅Me₅)Ta(B₂H₆)₂]₂ (X = Cl or Br) containing the *arachno*-B₂H₆²⁻ anion, by the reaction of [(η^5 -C₅Me₅)TaX₂]₂ with LiBH₄, has been viewed as a model for the dehydrodimerization reaction linking the analogous hydrocarbons CH₄ and C₂H₆.⁷

Particular attention has focused on the possibility that the methyl ligand alters its mode of co-ordination to a metal centre by involvement of terminal C–H bonds in a manner akin to the versatile co-ordination geometry of the tetrahydroborate group.⁸ For example, the compound [Ti(BH₄)₃(PMe₃)₂], featuring two distorted 'side-on' co-ordinated BH₄ groups, has been seen as a model for the 'agostic' methyl intermediates thought to be important in Ziegler–Natta catalysis.⁹

In addition to the various modes of ligation established for mononuclear species,⁸ at least five different co-ordination geometries are known for BH₄ groups bridging two or more metal centres.^{10–15} Metal tetrahydroborates therefore have the potential to adopt in the condensed phases polymeric or oligomeric structures in which hitherto unco-ordinated hydrogen atoms interact with adjacent metal centres forming intermolecular bridges and increasing the co-ordination numbers of these centres. Hydrocarbon ligands also show a tendency to bridge metal centres. Familiar examples which have been characterized structurally include methyl derivatives with μ_2 , *e.g.* [(η^5 -C₅Me₅)₂Sm(μ -Me)AlMe₂(μ -Me)₂Sm(η^5 -C₅Me₅)₂]¹⁶ and [(η^5 -C₅Me₅)₂Yb(μ -Me)Be(η^5 -C₅Me₅)]¹⁷ and even μ_3 , *e.g.* (MeLi)₄,¹⁸ methyl bridges.

In the case of metal centres bearing both methyl and tetrahydroborate groups there exists the possibility of intermolecular interaction *via* either ligand. Thus, solid [MeZnBH₄] has a polymeric structure in which terminal MeZn units are bridged by bis(bidentate) BH₄ groups,¹⁴ whereas [(MeBeBH₄)₂] is a methyl-bridged dimer featuring two terminal BH₄ lig-

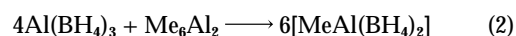
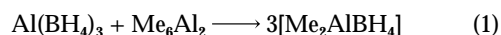
ands.^{19,20} With such considerations in mind, we set out to investigate the structures of solid Al(BH₄)₃, [MeAl(BH₄)₂] and [Me₂AlBH₄], principally through X-ray diffraction of single crystals at low temperatures, seeking to elucidate structural trends for the series [Me_xAl(BH₄)_{3-x}] (*x* = 0–3).

Experimental

Synthesis

Aluminium tris(tetrahydroborate) was prepared from AlCl₃ and LiBH₄ by the method of Schlesinger *et al.*²¹ Fractionation *in vacuo* gave samples judged to be pure on the basis of IR and ¹H and ¹¹B NMR measurements.^{22,23}

Dimethylaluminium tetrahydroborate and methylaluminium bis(tetrahydroborate) were prepared *via* reactions (1) and (2),



respectively.^{24,25} In a typical experiment, Me₆Al₂ and Al(BH₄)₃ in the appropriate proportions were co-condensed in an all-glass ampoule equipped with a constriction and a break-seal. After sealing the constriction the reaction mixture was maintained at room temperature for *ca.* 4 h. The [Me₂AlBH₄] or [MeAl(BH₄)₂] so produced was then purified by fractionation *in vacuo* in all-glass apparatus. In the case of [Me₂AlBH₄] the product collected as a white crystalline solid in a trap cooled to –51 °C. The more volatile [MeAl(BH₄)₂] could be collected as a glassy solid involatile at –126 °C. The purity of individual samples of both compounds was assessed by measurement of the IR spectra of solid films and of the vapour and by reference also to the ¹¹B and ¹H NMR spectra of solutions in [²H₈]toluene.^{24,26}

Samples of all three compounds were loaded into Pyrex capillaries each of *ca.* 0.5 mm internal diameter for the purpose of crystal growth. Invariably, the first step involved rigorous preconditioning of the capillary by exposure to the sample

vapour for 1–2 h prior to re-evacuation; this served to scavenge any residual moisture adsorbed on the glass surfaces. Approximately 0.01 cm³ of each compound was then transferred from the storage ampoule and condensed in the neck of the vessel; with careful warming, the material was caused to melt and run down to the bottom of the capillary. Typically a column of liquid 1.5–2 cm in depth was required. Once this had been achieved the sample was cooled to –196 °C and the capillary sealed such that its total length did not exceed 3 cm.

Growth of crystals for X-ray diffraction

Since each of the compounds is liquid at ambient temperatures, single crystals were grown by careful cooling, with the sample held in a capillary mounted on the diffractometer.²⁷ Capillaries were secured with Araldite glue in a thermally insulating Tufnol pip which was then fixed to a goniometer head and mounted in the cold stream of an Oxford Cryosystems low-temperature device attached to a Stöe Stadi-4 four-circle diffractometer.²⁸ A stable solid–liquid phase boundary was then established within the sample, and crystal growth effected by slow cooling at approximately 5 K h^{–1}. For compounds with more than one solid phase, growth of crystals *via* this method gives access only to the high-temperature form. In order to obtain a single crystal of the phase stable at lower temperatures, the entire sample was frozen to a temperature below the transition temperature and a crystal then grown by zone-refining techniques.²⁹ In practice, this involved holding a thin, heated copper wire against the capillary, creating a very steep temperature gradient in the sample. Adjustment of the position of the wire created a mobile liquid zone, behind which a single crystal could grow. The quality of crystals grown in this way was found to be inferior to that of crystals grown by the simpler slow-cooling method.

(a) **Dimethylaluminium tetrahydroborate.** A single crystal of [Me₂AlBH₄] was grown from the solid–liquid phase boundary by cooling from 287 K.

(b) **Methylaluminium bis(tetrahydroborate).** It proved impossible to obtain single crystals of [MeAl(BH₄)₂] using either slow-cooling or zone-refining techniques. Solid [MeAl(BH₄)₂] appears to be an amorphous glass and it proved difficult even to define a melting point.

(c) **Aluminium tris(tetrahydroborate).** A single crystal of Al(BH₄)₃ was grown initially from the solid–liquid phase boundary by slow cooling from 210 K, and then cooled to 180 K to begin data collection. Over a period of 30–45 min, however, the intensities of the standard reflections declined steadily. Investigation by oscillation photography of further crystals grown in this manner confirmed that these, too, lost crystallinity over a period of 1 h at 180 K. Cooling the crystal to 110 rather than 180 K resulted in much more rapid loss of crystallinity. These findings suggested that a phase change occurs in the temperature range 180–210 K, with the β phase formed by cooling the liquid changing slowly to the low-temperature α form. In order to elaborate on this possibility, crystals were subsequently cooled only to 195 K, conditions allowing the collection of a data set for the β phase if the transition temperature lies in the range 195–180 K. In the event this proved to be the case. A crystal of the low-temperature α phase was grown using zone-refining techniques at 150 K.

Crystallography

Crystal data. (a) *Dimethylaluminium tetrahydroborate.* C₂H₁₀AlB, *M* = 143.78, orthorhombic, space group *Pbca*, *a* = 10.029(6), *b* = 12.401(4), *c* = 17.947(9) Å, *U* = 2232(2) Å³,

$\lambda = 0.710\ 73\ \text{\AA}$, *Z* = 8, *D*_c = 0.865 g cm^{–3}, *F*(000) = 640, *T* = 110 K, colourless crystal 0.80 × 0.40 × 0.40 mm, μ(Mo-Kα) = 0.190 mm^{–1}.

(b) *Aluminium tris(tetrahydroborate), α form.* H₁₂AlB₃, *M* = 71.51, monoclinic, space group *C2/c*, *a* = 21.917(4), *b* = 5.986(1), *c* = 21.787(4) Å, β = 111.90(3)°, *U* = 2652.1(9) Å³, λ = 0.710 73 Å, *Z* = 16, *D*_c = 0.716 g cm^{–3}, *T* = 150 K, colourless crystal 0.80 × 0.30 × 0.30 mm, μ(Mo-Kα) = 0.152 mm^{–1}.

(c) *Aluminium tris(tetrahydroborate), β form.* H₁₂AlB₃, *M* = 71.51, orthorhombic, space group *Pna2₁*, *a* = 18.021(3), *b* = 6.138(2), *c* = 6.1987(14) Å, *U* = 685.7(3) Å³, λ = 0.710 73 Å, *Z* = 4, *D*_c = 0.693 g cm^{–3}, *T* = 195 K, colourless crystal 0.80 × 0.30 × 0.30 mm, μ(Mo-Kα) = 0.147 mm^{–1}.

Data collection. All data were collected on a Stöe Stadi-4 four-circle diffractometer with graphite-monochromated Mo-Kα radiation, ω–2θ mode.

(a) *Dimethylaluminium tetrahydroborate.* Of the 1746 reflections measured (θ_{max} = 24.97°; 0 ≤ *h* ≤ 10, 0 ≤ *k* ≤ 14, 0 ≤ *l* ≤ 21), 1699 were unique (*R*_{int} = 0.133). An absorption correction was applied with ψ-scan data (*T*_{min} = 0.660, *T*_{max} = 0.744).

(b) *Aluminium tris(tetrahydroborate), α form.* Of the 1477 reflections measured (θ_{max} = 20.00°; –17 ≤ *h* ≤ 26, –6 ≤ *k* ≤ 0, –19 ≤ *l* ≤ 23), 1233 were unique (*R*_{int} = 0.236). No absorption correction was applied.

(c) *Aluminium tris(tetrahydroborate), β form.* Of the 767 reflections measured (θ_{max} = 22.47°; –1 ≤ *h* ≤ 19, –1 ≤ *k* ≤ 6, –1 ≤ *l* ≤ 6), 598 were unique (*R*_{int} = 0.034). No absorption correction was applied.

Structure solution and refinement. (a) *Dimethylaluminium tetrahydroborate.* The crystal structure was solved using direct methods (SHELXTL³⁰) and refined by full-matrix least squares with anisotropic displacement parameters for all non-hydrogen atoms. Methyl hydrogens were located in a difference synthesis performed about the loci of possible hydrogen-atom positions; in subsequent cycles of least-squares refinement the methyl groups were treated as rigid rotating groups [*r*(C–H) = 0.96 Å]. All hydrogen atoms attached to boron were located in difference syntheses and allowed to refine freely. At convergence the ‘conventional’ *R*1 stood at 0.063 [based on *F* and 1080 data with *F* > 4σ(*F*)] and *wR*2 = 0.1631 (based on *F*² and all 1685 data used for refinement) for 102 parameters. The final Δ*F*-synthesis maximum and minimum were 0.30 and –0.29 e Å^{–3}, respectively. The weighting scheme used was of the form *w* = 1/[σ²(*F*_o²) + (*aP*)² + *bP*], where *P* = [*F*_o² + 2*F*_c²]/3, *a* = 0.0677 and *b* = 1.09.

(b) *Aluminium tris(tetrahydroborate).* The crystal structure of the high-temperature (β) phase was solved by direct methods (SIR 92³¹), while that of the low-temperature (α) phase was solved for the aluminium atom using Patterson methods (SHELXTL³⁰). The refinement was as above. All hydrogen atoms attached to boron were located in difference syntheses; in the β phase the positional parameters were refined freely and common isotropic thermal parameters refined for chemically similar atoms, whereas in the α phase similarity restraints were applied to chemically equivalent bonds. For the α form *R*1 = 0.086 (based on 508 data) and *wR*2 = 0.1697 (1054 data) for 150 parameters, while for the β form *R*1 = 0.042 (449 data) and *wR*2 = 0.0830 (598 data) for 76 parameters. The final Δ*F*-synthesis maxima and minima were 0.24 and –0.30 and 0.17 and –0.15 e Å^{–3}, respectively. The weighting schemes used were as above with *a* = 0.0584 and *b* = 0.000 for the α form and *a* = 0.000 and *b* = 0.43 for the β form.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/404.

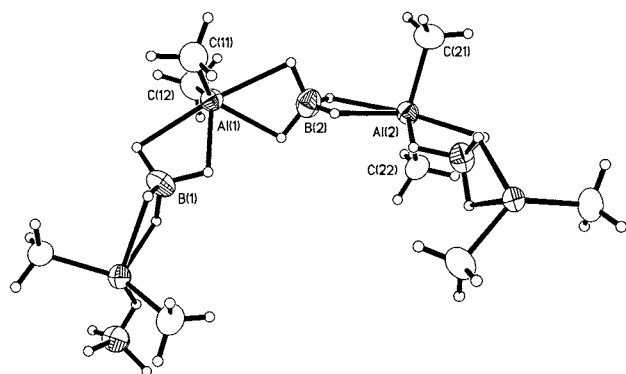


Fig. 1 Crystal structure of $[\text{Me}_2\text{AlBH}_4]$ at 150 K

Table 1 Bond distances (Å) and angles ($^\circ$) for crystalline $[\text{Me}_2\text{AlBH}_4]$ at 150 K *

Al(1)–C(12)	1.912(5)	Al(1)–H(21)	1.97(5)
Al(1)–C(11)	1.926(5)	Al(2)–H(22)	1.91(5)
Al(1) \cdots B(1)	2.419(6)	Al(2)–H(23)	2.22(5)
Al(1) \cdots B(2)	2.392(6)	Al(1)–H(24)	2.15(5)
Al(2') \cdots B(1)	2.423(6)	B(1)–H(11)	1.12(5)
Al(1)–H(11)	2.15(5)	B(1)–H(12)	1.17(4)
Al(1)–H(12)	1.82(4)	B(1)–H(13)	1.16(5)
Al(2)–H(13)	1.83(5)	B(1)–H(14)	1.07(5)
Al(2)–H(14)	2.15(5)	C(11)–H(11A)	0.98
C(12)–Al(1)–C(11)	130.5(2)	Al(1)–B(1)–H(12)	46(2)
C(12)–Al(1)–B(2)	99.3(2)	Al(2')–B(1)–H(12)	127(2)
C(11)–Al(1)–B(2)	106.9(2)	Al(1)–B(1)–H(13)	127(2)
C(12)–Al(1)–B(1)	105.7(2)	Al(2')–B(1)–H(13)	47(2)
C(11)–Al(1)–B(1)	96.5(2)	Al(1)–B(1)–H(14)	122(2)
C(11)–Al(1)–H(12)	102.7(14)	Al(2')–B(1)–H(14)	63(2)
C(11)–Al(1)–H(21)	123.7(14)	H(11)–B(1)–H(12)	109(3)
B(1)–Al(1)–H(21)	95.1(14)	H(11)–B(1)–H(13)	111(3)
B(2)–Al(1)–H(12)	93(2)	H(11)–B(1)–H(14)	113(4)
H(12)–Al(1)–H(21)	69(2)	H(12)–B(1)–H(13)	108(3)
B(1)–Al(1)–B(2)	119.9(2)	H(12)–B(1)–H(14)	108(3)
Al(1)–B(1)–Al(2')	171.8(3)	H(13)–B(1)–H(14)	109(3)
Al(1)–B(1)–H(11)	63(2)	Al(1)–C(11)–H(11A)	109.5(2)
Al(2')–B(1)–H(11)	123(2)	H(11A)–C(11)–H(11B)	109.5

* Symmetry operation: single prime, $-x, y - \frac{1}{2}, -z + \frac{1}{2}$.

Table 2 Comparison of selected bond lengths (Å) and angles ($^\circ$) for $[\text{Me}_2\text{AlBH}_4]$, $\text{Be}(\text{BH}_4)_2$ and $[\text{MeZnBH}_4]$

Parameter	$[\text{Me}_2\text{AlBH}_4]$		$\text{Be}(\text{BH}_4)_2$ Solid	$[\text{MeZnBH}_4]$ Solid
	Solid	Vapour		
B–H	1.07(5)– 1.17(4)	1.21(2)– 1.23(2)	1.08(2)– 1.17(3)	1.32(4)– 1.36(5)
M \cdots B	2.419(6), 2.392(6)	2.128(8)	2.001(4), 1.999(5)	2.30(2)– 2.32(2)
M–H	1.82(4), 2.22(5)	1.77(3)	1.59(2)– 1.65(2)	1.81(5), 1.82(5)
Covalent radius of metal atom ^b	1.26	1.26	1.06	1.31
H–B–H	108(3)– 113(3)	113(4), 116 ^c	109(2)– 112(2)	103(3)– 115(4)
M–B–M	171.8(3)	<i>d</i>	175.4(7)	171.9(3)
B–M–B	119.9(2)	<i>d</i>	111.7	98.6(7)
Ref.	This work	34	32	14

^a Parameters relate to the BH_4 units within the helical chain. ^b See ref. 33. ^c Fixed. ^d Not applicable.

Results and Discussion

Crystal structure of dimethylaluminium tetrahydroborate at 150 K

The structure of $[\text{Me}_2\text{AlBH}_4]$ at 110 K is illustrated in Fig. 1. Bond distances and angles are listed in Table 1. The results show that solid dimethylaluminium tetrahydroborate consists of helical polymers in which dimethylaluminium units are linked by BH_4 groups exhibiting bidentate ligation with respect to each of the adjacent metal atoms. In this respect, the structure resembles closely those of beryllium bis(tetrahydroborate)³² and methylzinc tetrahydroborate.¹⁴ Comparative parameters for these three compounds are set out in Table 2. The beryllium atom in $\text{Be}(\text{BH}_4)_2$ is bonded to six bridging hydrogen atoms, these being arranged to give trigonal-prismatic co-ordination of the central metal atom.³² The aluminium centre in $[\text{Me}_2\text{AlBH}_4]$ is also six-co-ordinated, being bonded to four bridging hydrogen atoms and two methyl groups. An ideal octahedral model for the aluminium co-ordination sphere is what would be expected if highly directional covalent bonding were dominant. The opening out of the C–Al–C angle (from 118 to 130 $^\circ$) on going from the vapour to the solid is, however, consistent with the significantly ionic model of the solid described below. Consequently, it might be more fruitful to consider the solid to be based around a trigonal-planar AlC_2B framework. Distortion of the $\text{Al}(\text{H}_b)_4$ unit from the planar geometry implicit in octahedral co-ordination is small; the $\text{Al}(\mu\text{-H})_2\text{B}$ bridges are quite asymmetric with Al–H distances falling into two ranges above and below 2 Å, although the relatively large standard deviations on these parameters preclude a detailed analysis.

Whereas the helical polymeric skeletons of solid $\text{Be}(\text{BH}_4)_2$ ³² and $[\text{MeZnBH}_4]$ ¹⁴ spiral around 4₁ and 3₁ axes, respectively, $[\text{Me}_2\text{AlBH}_4]$ is disposed around a 2₁ crystallographic screw axis, albeit with two molecules in the asymmetric unit. In all three compounds the M–B–M angle is close to 180 $^\circ$ and the departure from linearity probably reflects contrasting co-ordination geometries at the metal atom. The B–M–B angles are 119.9(2), 111.7(4) and 98.6(7) $^\circ$ for $[\text{Me}_2\text{AlBH}_4]$, $\text{Be}(\text{BH}_4)_2$ ³² and $[\text{MeZnBH}_4]$,¹⁴ respectively.

In addition, the crystal structure of $[\text{Me}_2\text{AlBH}_4]$ reveals an interaction between the metal centre and BH_4 ligand which is considerably weaker than that in $[\text{MeZnBH}_4]$ ¹⁴ but similar to that associated with the more ionic condition prevailing in $\text{Be}(\text{BH}_4)_2$.³² Thus, the B–H distances in $[\text{Me}_2\text{AlBH}_4]$ and $\text{Be}(\text{BH}_4)_2$ are 1.07(5)–1.17(4) and 1.08(2)–1.17(3) Å, respectively, whereas those in $[\text{MeZnBH}_4]$ are 1.32(4) and 1.36(5) Å. Furthermore, the H–B–H angles show smaller distortions from the idealized tetrahedral values than do those in $[\text{MeZnBH}_4]$, although the estimated standard deviations in each case are in the order of 3 $^\circ$. The Al \cdots B distances [2.392(6) and 2.419(6) Å] are also indicative of weaker M \cdots BH_4 interactions; the corresponding value for $[\text{MeZnBH}_4]$ is 2.30(2) Å,¹⁴ despite the fact that the covalent radius of zinc (1.31 Å) is slightly larger than that of aluminium (1.26 Å).³³

Comparison of the structure of solid $[\text{Me}_2\text{AlBH}_4]$ with that of the gaseous molecule³⁴ reveals several differences consistent with the change from a discrete molecular structure to a polymer incorporating alternate $[\text{Me}_2\text{Al}]^+$ and $[\text{BH}_4]^-$ ions. Thus, the Al \cdots B and Al–H distances are appreciably longer in the solid phase [2.392(6), 2.419(6) and 1.82(4)–2.22(5) Å] than in the vapour [2.128(8) and 1.77(3) Å],³⁴ and the C–Al–C angle opens up from 118.4(7) $^\circ$ (for the vapour)³⁴ to 130.5(2) $^\circ$ (for the solid). These structural variations are also consistent with changes occurring in the IR and Raman spectra on condensation.^{26,34} For example, the opening out of the C–Al–C angle is predicted on the basis of changes in the relative intensities in infrared absorption of the symmetric and antisymmetric Al–C stretching vibrations.^{26,34} Furthermore, a strong band at 2194 cm^{-1} in the infrared spectrum of solid $[\text{Me}_2\text{AlBH}_4]$ can be

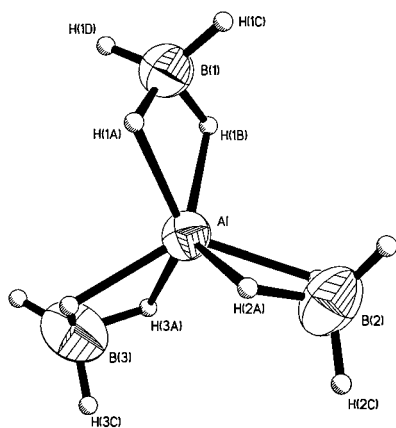


Fig. 2 Molecular structure of $\text{Al}(\text{BH}_4)_3$, as determined by X-ray diffraction of a crystalline sample of the β phase at 195 K

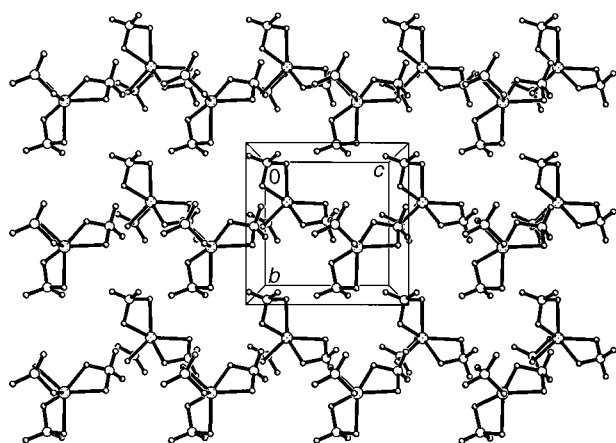


Fig. 3 Packing of the $\text{Al}(\text{BH}_4)_3$ units in the β phase of solid aluminium tris(tetrahydroborate) at 195 K

attributed to the stretching of B–H bonds within the semi-ionic polymer backbone.^{26,34} The wavenumber of such a band could be explained either in terms of the antisymmetric B–H stretching vibration of a slightly distorted BH_4^- ion or in terms of an antisymmetric B–H_b stretching vibration of an $\text{Al}(\mu\text{-H})_2\text{B}(\mu\text{-H})_2\text{Al}$ unit.

The structure of solid $[\text{Me}_2\text{AlBH}_4]$ is highly unusual in featuring a BH_4 group bridging two Group 13 metal centres. The only other compound exhibiting a similar structural unit is solid $[\text{H}_2\text{GaBH}_4]$, which incorporates two distinct types of bridging BH_4 group. One linkage features a $\text{Ga}(\mu\text{-H})_2\text{B}$ moiety with dimensions very similar to those of the $\text{Al}(\mu\text{-H})_2\text{B}$ unit in solid $[\text{Me}_2\text{AlBH}_4]$; the other features GaH_2 units bridged by bis(monodentate) $(\mu\text{-H})\text{BH}_2(\mu\text{-H})$ groups.³⁵ Bridging between gallium and boron atoms *via* a single hydrogen atom gives rise to an $\text{M}\cdots\text{B}$ distance (2.46–2.49 Å)³⁵ somewhat longer than is found in $[\text{Me}_2\text{AlBH}_4]$ [2.419(6), 2.392(6) Å], despite the extremely similar covalent radii of aluminium and gallium.³³ It is interesting that, whereas the aluminium centre in solid $[\text{Me}_2\text{AlBH}_4]$ exploits all four hydrogens of the BH_4 ligand in order to increase its co-ordination number to six, one of the gallium centres in solid $[\text{H}_2\text{GaBH}_4]$ retains the approximately tetrahedral, four-co-ordinate geometry seen in the vapour phase, with the consequence that each BH_4 ligand bears two terminal hydrogen atoms.³⁵ This difference in co-ordination geometries is consistent with the structural properties of many other aluminium and gallium compounds, for example solid AlCl_3 and GaCl_3 .³⁶ In both $[\text{MeZnBH}_4]$ ¹⁴ and $[\text{H}_2\text{GaBH}_4]$ ³⁵ directional covalent bonding appears to be more important than in $[\text{Me}_2\text{AlBH}_4]$; presumably this reflects the more polarizing nature of the post-transition metal centre.

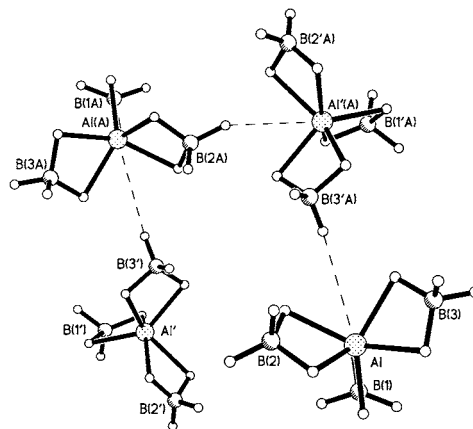


Fig. 4 View along the b axis of the α phase of solid $\text{Al}(\text{BH}_4)_3$

Table 3 Comparison of the bond lengths (Å) and angles (°) obtained for the α and β phases of solid $\text{Al}(\text{BH}_4)_3$ by X-ray diffraction with the parameters deduced for the gaseous molecule by electron diffraction and those calculated by *ab initio* methods

Parameter	X-Ray diffraction		Electron diffraction ^a	<i>Ab initio</i> calculation (MP2 level) ^b
	α phase	β phase		
Al–B	2.10(2)– 2.14(2)	2.10(1)– 2.13(1)	2.143(3)	2.149
Al–H _b	1.73(4)– 1.76(4)	1.67(5)– 1.75(4)	1.801(6)	1.752
B–H _b	1.13(4)– 1.14(4)	1.12(3)– 1.14(3)	1.283(12)	1.270
B–H _t	0.99(4), 1.01(4)	0.99(3), 0.99(3)	1.196(12)	1.194
B–Al–B	119.2(7)– 121.1(7)	118.7(4)– 122.5(4)	120	120
H _b –Al–H _b	65(2)	63(2)– 65(2)	73.4(8)	72.4
H _b –B–H _b	109(4)– 112(3)	106(3), 109(3)	114.0(2)	109.2
H _t –B–H _t	102(9)– 123(10)	123(4), 129(5)	116.2(22)	121.2
H _b –B–H _t	101(8), 120(8)	108(5)	<i>c</i>	<i>c</i>
θ^d	90.3(8)	89.5(6)	72.8(24)	66.8

^a From ref. 37. ^b From ref. 38. ^c Not given. ^d Taken as the angle between the planes defined by Al, B(1), B(2) and Al, H(1A), B(1) (see Fig. 2).

Crystal structures of aluminium tris(tetrahydroborate) at 195 and 150 K

The molecular structure of $\text{Al}(\text{BH}_4)_3$ at 195 K (that is, for the β phase) is illustrated in Fig. 2 and a packing diagram is shown in Fig. 3. The view along the b axis for the more densely packed α phase at 150 K is reproduced in Fig. 4. Bond distances and angles for both phases are listed in Table 3.

The crystal structures of both phases of aluminium tris(tetrahydroborate) are made up of discrete molecular $\text{Al}(\text{BH}_4)_3$ units. The geometry of the $\text{Al}(\text{BH}_4)_3$ molecule itself varies little between the two phases, the most significant differences affecting the $\text{B}(\text{H}_t)_2$ angles, which appear to be less uniform in the α phase. The poorer quality of the results accumulated for this phase is reflected in the larger standard deviations quoted, particularly for parameters involving bonds to hydrogen atoms.

The principal difference between the α and β phases relates to the *packing* of the molecular units. In the β phase there are two 'nearest neighbour' molecules positioned above and below the triangular faces of the trigonal-prismatic $\text{Al}(\mu\text{-H})_6$ unit such that the shortest $\text{Al}\cdots\text{H}$ distances are 3.6 Å. By contrast, in the α phase there is only one such 'nearest neighbour', with the asymmetric units spiralling around a 2₁ axis, as shown in Fig. 4.

Although the existence of any significant secondary interaction can be ruled out, the spiralling of $\text{Al}(\text{BH}_4)_3$ units around a crystallographic screw axis is intriguing in mirroring the behaviour of compounds such as $[\text{MeZnBH}_4]_n$,¹⁴ $\text{Be}(\text{BH}_4)_2$,³² and $[\text{Me}_2\text{AlBH}_4]$.

The electron-diffraction pattern of $\text{Al}(\text{BH}_4)_3$ in the vapour phase³⁷ confirms the planar AlB_3 skeleton and bidentate co-ordination of the BH_4 ligands implied by vibrational spectroscopy,²² but analysis fails to differentiate between D_{3h} and D_3 structural models. For the D_3 model an angle, θ , of $72.8(24)^\circ$ between the AlB_2 and $\text{Al}(\mu\text{-H})\text{B}$ planes was found to give the best account of the experimental scattering.³⁷ Subsequent *ab initio* calculations have suggested that the D_{3h} structure is a transition state between two minima of D_3 symmetry, with the energy minimum occurring for $\theta = 66.8^\circ$.^{38,39} The corresponding angles in the α and β phases of the solid (90.3 and 89.5° , respectively) conform within the limits of experimental error to 90° . Clearly the possibility that crystal-packing forces play a relatively important role in fixing this structural parameter complicates comparisons with the gaseous molecule, particularly as the barrier predicted for synchronous rotation of the three BH_4 groups is extremely low ($0.8\text{--}3.7$ kJ mol⁻¹).³⁸

The B-H_i and B-H_b bond lengths are very similar to those found in the $[\text{Al}(\text{BH}_4)_4]^-$ ion [$0.95(5)\text{--}1.22(5)$ and $0.80(5)\text{--}1.07(5)$ Å, respectively],⁴⁰ differences in the Al-H and $\text{Al}\cdots\text{B}$ distances between the two species and the existence of less symmetrical $\text{Al}(\mu\text{-H})_2\text{B}$ bridges in $[\text{Al}(\text{BH}_4)_4]^-$ almost certainly reflect the greater steric congestion and distorted dodecahedral geometry peculiar to the anion.⁴⁰ The molecular structure of $\text{Al}(\text{BH}_4)_3\cdot\text{NMe}_3$ contains seven-co-ordinated aluminium, the NMe_3 ligand and six bridging hydrogens adopting a distorted pentagonal-bipyramidal geometry.⁴¹ The $\text{Al}\cdots\text{B}$ distances for this complex [$2.23(1)$ Å] are similar to those observed for both phases of $\text{Al}(\text{BH}_4)_3$. However, the Al-H [$1.97(11)$ Å], B-H_b [$1.43(11)$ Å] and B-H_i bond lengths [$1.19(11)$ Å] are significantly longer than those displayed by either $\text{Al}(\text{BH}_4)_3$ or $[\text{Al}(\text{BH}_4)_4]^-$; ^{40,41} this almost certainly reflects the large errors in the lengths of bonds to hydrogen atoms implicit in the photographic methods used.⁴¹

Given the disposition of $[\text{Me}_2\text{AlBH}_4]$ to form a polymeric, semi-ionic structure in the solid state and that of $\text{Al}(\text{BH}_4)_3$ to remain as discrete molecular units, the structure of the intermediate compound $[\text{MeAl}(\text{BH}_4)_2]$ would be of considerable interest. Vibrational studies imply that $[\text{MeAl}(\text{BH}_4)_2]$ undergoes a significant change of structure with the transition from the vapour to the solid phase.^{26,42} Indeed, a strong band found at 2235 cm⁻¹ in the infrared spectrum of the solid, which is absent in the spectrum of the vapour, is reminiscent of features attributable to the stretching motions of B-H bonds within the polymeric chains of $[\text{Me}_2\text{AlBH}_4]$,^{26,34} $[\text{MeZnBH}_4]$ ¹⁴ and $\text{Be}(\text{BH}_4)_2$.³² That the volatilities of $[\text{MeAl}(\text{BH}_4)_2]$,^{26,42} and $\text{Al}(\text{BH}_4)_3$ ⁴⁴ should be similar (compared with the much lower volatility of $[\text{Me}_2\text{AlBH}_4]$ ²⁶) tends, on the other hand, to argue against a structure for $[\text{MeAl}(\text{BH}_4)_2]$ in the solid state involving significant aggregation of the molecular units. It is unfortunate, therefore, that the solid monomethylaluminium compound is a glass with no definite melting point, although this fact in itself implies that there are only small energy differences between various possible structures.

Several factors appear to influence the structural changes occurring for the series $[\text{Me}_x\text{Al}(\text{BH}_4)_{3-x}]$. Most obvious is the ability of BH_4 , but not CH_3 , to act as a bidentate ligand and thereby occupy two co-ordination sites at the metal; this allows $\text{Al}(\text{BH}_4)_3$ to retain its discrete molecular nature in the solid state, whereas ' Me_3Al ' dimerizes to give Me_6Al_2 .⁴⁵ A polymeric structure for solid $\text{Al}(\text{BH}_4)_3$ featuring bis(bidentate) BH_4 groups would imply an eight-co-ordinate geometry at the aluminium centre, and, although such a geometry finds precedent in the $[\text{Al}(\text{BH}_4)_4]^-$ anion,⁴⁰ there is little suggestion of any significant secondary interaction in either the α or the β phase of

$\text{Al}(\text{BH}_4)_3$. Progressing from Me_6Al_2 to $[\text{Me}_2\text{AlBH}_4]$ witnesses a change from methyl- to tetrahydroborate-bridged aggregation. The bonding of the BH_4 group to each metal centre *via* two bridging hydrogens adapts itself to an increase in co-ordination number from four for the gaseous Me_2AlBH_4 molecule to six in the solid. This contrasts with the situation in the analogous beryllium compounds dimethylberyllium and methylberyllium tetrahydroborate,^{19,20,46} both of which display methyl-bridged structures. Presumably this reflects the fact that bridging *via* methyl groups requires closer approach of the two metal atoms, a condition which is facilitated by the small size of beryllium, even if it is doubtful whether metal-metal bonding comes into play; by contrast, bridging *via* BH_4 ligands permits the larger aluminium atom to achieve six-fold co-ordination without the need for close metal-metal contacts.

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