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Methylzinc tetrahydroborate: physical and chemical properties and crystal structure at low temperature†

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Methylzinc tetrahydroborate, $MeZnBH_4$, has been prepared by two routes and initially characterized by elemental analysis and its spectroscopic properties. The structure has been determined by X-ray crystallography at 150 K [trigonal, space group $R\bar{3}c$, $a = b = 15.831(10)$, $c = 8.36(2)$ Å, $Z = 18$, $R = 0.072$] to reveal helical polymers in which $MeZn^+$ and BH_4^- units alternate, with the latter functioning as a bidentate ligand with respect to both of the adjacent metal atoms. It thus resembles the structure of solid $Be(BH_4)_2$ with the difference that the zinc is five-co-ordinated, the Me and H ligands adopting a distorted square-pyramidal geometry. Chemical properties of methylzinc tetrahydroborate investigated include its thermal decomposition and its reactions with ammonia, dimethyl sulfide, triphenylphosphine and CO; disproportionation into Me_2Zn and $Zn(BH_4)_2$ appears to be a common feature of its chemistry.

Metal tetrahydroborates are noteworthy for several reasons. From a practical standpoint, they may be suitable as precursors to the metal itself,[1a] as well as to hydride,[1b] boride[1c] or alkyl[1d] derivatives; hence they may be source materials for chemical vapour deposition processes leading to metallic or semiconductor materials. Metal tetrahydroborates have also attracted numerous structural studies,[2–8] which have revealed a remarkable versatility on the part of the tetrahydroborate ion, BH_4^-, with regard to the mode of its ligation to the metal centre. In addition to those compounds exhibiting essentially ionic structures,[9] there exist numerous well characterized derivatives in which the metal centre is linked to the tetrahydroborate group through one,[2] two[3,10,11] or three[4] bridging hydrogen atoms. The energy differences between the different modes of ligation have been shown to be small, the configuration adopted depending on both steric and electronic effects.[12–14] Furthermore, compounds such as Me_2AlBH_4[15,16] and $Be(BH_4)_2$[17–19] have been shown to exhibit different modes of ligation of the BH_4^- group in different phases. The structures of many tetrahydroborate derivatives in the vapour phase have been probed by vibrational spectroscopy and by electron-diffraction studies,[4,8,11,15,20] although the scope of structure determination in the solid phase has been limited by the difficulty of locating hydrogen atoms in close proximity to a metal atom on the basis of X-ray diffraction experiments.

Of the Group 12 tetrahydroborates, $Zn(BH_4)_2$ and $Cd(BH_4)_2$ have both been synthesized from $LiBH_4$ and the corresponding metal chloride,[21–23] although little has been established about the structures of either of these compounds in the solid phase. Similarly, the volatile, white solid methylzinc tetrahydroborate, $MeZnBH_4$, has received relatively little attention since an initial report of its synthesis by Ridley in 1965.[24] Elemental analysis of the compound, estimation of reacting proportions and examination of the infrared spectra of the volatile products led Ridley to postulate that its synthesis can be accomplished *via* reaction (1). Nibler and Cook[25]

$$2ZnMe_2 + B_2H_6 \longrightarrow BMe_3 + MeZnBH_4 + ZnH_2 \quad (1)$$

investigated the structure of solid methylzinc tetrahydroborate by examination of the infrared and Raman spectra of thin films of normal and deuteriated forms deposited on a CsI window at 12 K. On the basis of spectra containing no strong bands in the regions characteristic of the stretching modes of *either* terminal or bridging B–H bonds of a covalently bound BH_4 group, the solid was judged to be an ionic polymer involving more-or-less discrete $MeZn^+$ and BH_4^- ions, with a structure similar to that of $Be(BH_4)_2$.[17]

We now report the crystal structure of methylzinc tetrahydroborate at low temperature (150 K); in addition, we describe an alternative synthetic route to the compound, as well as some of its physical and chemical properties.

Experimental

(*i*) General procedures and purification of reagents

Synthesis of methylzinc tetrahydroborate was accomplished using a conventional high-vacuum line incorporating greaseless valves equipped with Teflon keys and ground-glass joints lubricated with Voltalef 90 grease. Purification and manipulation of samples were then typically carried out using all-glass apparatus which was preconditioned by exposure to dimethylzinc vapour for several hours. Dimethylzinc and [$^2H_6$]dimethylzinc were prepared according to the method of Hota and Willis,[26] and diborane and [$^2H_6$]diborane by the reaction of sulfuric acid with sodium tetrahydroborate, as described by Schroeder *et al.*[27] Ammonia, as supplied by B.O.C., was dried by distillation from sodium; hydrogen chloride was supplied by Air Products. Dimethyl sulfide supplied by Aldrich was dried by refluxing over sodium metal, followed by fractional distillation in a dry nitrogen atmosphere. Each of these reagents was further purified by trap-to-trap distillation *in vacuo* prior to use. Carbon monoxide was used as received from B.O.C. Triphenylphosphine (Aldrich) was recrystallized from a mixture of diethyl ether and tetrahydrofuran, and lithium tetrahydroborate (also Aldrich) was recrystallized from diethyl ether prior to use. Reagents were then judged to be pure on the basis of infrared and/or NMR measurements. [$^2H_8$]Toluene (Aldrich) was dried by storage over type 4A molecular sieve prior to use. Elemental analyses were performed by the Analytische Laboratorien Elbach in Engelskirchen, Germany.

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† *Non-SI unit employed:* Torr ≈ 133 Pa.

(*ii*) Physical measurements

Infrared spectra were recorded between 400 and 4000 cm^{-1} using a Mattson Galaxy FT-IR spectrometer operating at a resolution down to 0.5 cm^{-1}. Solid samples were investigated in the form of discs formed by compressing a powdered sample with a ten-fold excess of dry, powdered KBr. Low-temperature measurements on solid samples were carried out with the aid of an infrared cell incorporating a CsI window cooled to 77 K on which the sample vapour, injected *via* a narrow glass inlet, could be condensed as a thin, polycrystalline film.

The NMR spectra were recorded on a Bruker FT model 300 spectrometer operating at 300 MHz for ^{1}H and 96.25 MHz for ^{11}B measurements. Typically, solutions at concentrations of *ca.* 1 mol dm^{-3} in dry [$^2H_8$]toluene were prepared in 5 mm Pyrex NMR tubes. Mass spectra were recorded on an AEI MS302 spectrometer equipped with an evacuable, all-glass inlet system and on a Hiden HAL/3F residual gas analyser.

(*iii*) Synthesis of methylzinc tetrahydroborate

(*a*) **From dimethylzinc and diborane.** Typically, a bulb (1 l) guarded by a Young's tap was conditioned by exposure to dimethylzinc vapour at *ca.* 20 Torr for 3 h, this serving to scavenge residual moisture retained by the Teflon and glass surfaces. After re-evacuation, diborane (typically 23 mg, 0.83 mmol) and a six-fold excess of dimethylzinc were allowed to react at room temperature over a period of 16 h. In accordance with Ridley's observations,[24] clusters of long, acicular crystals were observed to form. Trap-to-trap distillation of the volatile material *in vacuo* gave methylzinc tetrahydroborate as a white, polycrystalline solid involatile at −23 °C. Unchanged dimethylzinc was trapped at −95 °C; a more volatile fraction was shown by its IR spectrum to consist mainly of BMe_3,[28] together with unchanged diborane. Reaction times much longer than 24 h resulted in significant amounts of grey decomposition product, whereas much shorter reaction times resulted in relatively poor conversion and the recovery of large quantities of unchanged diborane.

In order to obtain a single crystal suitable for X-ray diffraction it was necessary to modify the apparatus substantially so as to counter the tendency of the crystals to decompose, even under very dry nitrogen. The resulting apparatus incorporated a bulb (1 l) to which a cold-finger was attached *via* a large 'Rotaflo' tap. Pyrex capillary side-arms *ca.* 0.3 mm in diameter and each containing a small quantity of Voltalef 90 grease were fused to the cold-finger. The apparatus was first rigorously preconditioned with dimethylzinc vapour. Crystals most suitable for X-ray diffraction were then formed by admitting dimethylzinc and diborane vapours to the main part of the bulb to pressures of 120 and 20 Torr, respectively. Crystals grown in this way were manipulated by the use of a pointed glass-coated stirrer bar until held firmly in place in one of the capillary side-arms.

(*b*) **From methylzinc chloride and lithium tetrahydroborate.** Typically, methylzinc chloride was prepared *in situ* by the reaction of dimethylzinc (150 mg, 1.59 mmol) with hydrogen chloride (44 mg, 1.2 mmol) at −23 °C. After the mixture had been left at room temperature for 2 h to ensure complete reaction, the methane (1.15 mmol) was determined using a Toepler pump and a quantity of dimethylzinc (0.4 mmol) was recovered. To the methylzinc chloride so formed was added $LiBH_4$ (100 mg, 4.5 mmol), and the solid mixture was stirred for 10 h at room temperature while volatile products were removed and trapped at −196 °C under continuous pumping. Fractionation of the volatile material gave methylzinc tetrahydroborate in overall yields of 10–15% based on equations (2) and (3) and on the amount of dimethylzinc consumed.

$$ZnMe_2 + HCl \longrightarrow MeZnCl + CH_4 \qquad (2)$$

$$MeZnCl + LiBH_4 \longrightarrow MeZnBH_4 + LiCl \qquad (3)$$

(*iv*) Reaction of methylzinc tetrahydroborate with ammonia

Ammonia (18 mg, 1.05 mmol) was co-condensed with methylzinc tetrahydroborate (19 mg, 0.2 mmol) and the reaction mixture was maintained at −78 °C for *ca.* 24 h. The excess of ammonia recovered at −78 °C (0.275 mmol) implied the formation at this temperature of an adduct with the composition $MeZnBH_4{\cdot}4NH_3$. The reaction vessel was then allowed to warm slowly to room temperature under continuous pumping. Warming to 0 °C led to the evolution of 0.114 mmol of dimethylzinc and a further 0.22 mmol of ammonia. There remained an involatile, white solid, the infrared spectrum of which showed bands at the following wavenumbers (in cm^{-1}; s = strong, m = medium, w = weak, sh = shoulder, br = broad): 3350s (br), 3267m (sh), 3252m, 3205m (sh), 2287s (sh), 2237s, 2171s (sh), 1739w, 1606m, 1263m (sh), 1246s, 1222s, 1125m, 1067m, 706s, 667m and 606w (sh) [Found: H, 12.75; B, 11.00; N, 41.40; Zn, 32.25. Calc. for $Zn(NH_3)_6(BH_4)_2$: H, 13.30; B, 10.95; N, 42.60; Zn, 33.15%].

The IR spectrum of the adduct initially formed at low temperatures was investigated by co-condensing the reagents on a CsI window at −196 °C, warming the window to −50 °C, and pumping away any unchanged ammonia. The spectrum showed bands at the following wavenumbers (in cm^{-1}): 3362m, 3311s, 3240m, 3205mw, 3165mw, 2924m, 2868w, 2332m, 2245s, 2177m, 1610m, 1263m (sh), 1244s, 1217m, 1178s, 1125m, 1101s, 715m, 657m and 549mw.

(*v*) Reaction of methylzinc tetrahydroborate with dimethyl sulfide

Dimethyl sulfide (62 mg, 1.0 mmol) was co-condensed with methylzinc tetrahydroborate (20 mg, 0.21 mmol) and the reaction mixture was warmed slowly to −23 °C. The methylzinc tetrahydroborate was observed to dissolve smoothly and, after 2 h at this temperature to ensure complete reaction, the excess of dimethyl sulfide was removed under continuous pumping. There remained in the reaction vessel a colourless viscous liquid which proved sufficiently volatile to be transferred under continuous pumping at room temperature. (The liquid had a vapour pressure of *ca.* 1 Torr under these conditions, as judged by its distillation properties.) The amount of dimethyl sulfide recovered (0.81 mmol) implied the formation of the 1 : 1 adduct $MeZnBH_4{\cdot}SMe_2$. Further characterization was achieved by measuring the infrared spectra (*i*) of the solid formed by condensation on a caesium iodide window held at 77 K and (*ii*) of the matrix-isolated species formed by co-condensation of the vapour with an excess of dinitrogen at 14 K, and by measuring the ^{1}H and ^{11}B NMR spectra of solutions in [$^2H_8$]toluene at −20 °C.

(*vi*) Reactions of methylzinc tetrahydroborate with triphenylphosphine and CO

In a typical experiment a [$^2H_8$]toluene solution containing $MeZnBH_4$ (0.5 mmol) and a 5–10-fold excess of either PPh_3 or CO was allowed to warm from −80 °C to room temperature in 10 °C steps, the progress of any reaction being monitored by measuring the ^{11}B and ^{1}H NMR spectra. In the case of the CO experiments no evidence of any resonance attributable to $OC{\cdot}BH_3$[29] was observed, even with samples maintained at 0 °C for a further week. Very weak resonances attributable to $Ph_3P{\cdot}BH_3$[30] appeared at δ_B 37.1 and δ_H 1.70 for samples maintained at 0 °C for several days, although the intensities of these signals relative to those due to unchanged $MeZnBH_4$ implied a conversion of less than 1%.

(*vii*) X-Ray diffraction of methylzinc tetrahydroborate crystals at low temperature

Several acicular crystals *ca.* 1 mm in length were loaded into hand-drawn Pyrex capillaries of approximately 0.3 mm internal diameter using the method described earlier. Initial investigation of several crystals by oscillation photography showed that these typically became amorphous over a period of 72 h, in keeping with the known thermal instability of the compound.[24] Consequently, following transfer of the crystal to a diffractometer, data collection was carried out at 150 K.

Crystal data. CH_7BZn, $M = 92.25$, trigonal, space group $R3c$, $a = b = 15.831(10)$, $c = 8.36(2)$ Å, $U = 1814(4)$ Å^3, $\lambda = 0.710\,73$ Å, $Z = 18$, $D_c = 1.569$ g cm^{-3}, $F(000) = 864$; colourless acicular crystal, 1.00 × 0.10 × 0.05 mm, μ(Mo-Kα) = 5.84 mm^{-1}.

Data collection. Data were collected on a Stoë Stadi-4 four-circle diffractometer with graphite-monochromated Mo-Kα X-radiation; ω–2θ mode, ω half width $(1.32 + 0.35 \tan\theta)^\circ$. Of the 1693 reflections measured ($\theta_{max} = 22.5^\circ$; $-9 \leqslant h \leqslant 16$, $-16 \leqslant k \leqslant 8$, $-8 \leqslant l \leqslant 8$), 502 were unique. An absorption correction was performed with ψ-scan data ($T_{min} = 0.736$, $T_{max} = 0.938$); $R_{int} = 0.085$. Variation of three intensity standards, measured every 60 min of X-ray exposure time, was no greater than 1.5%.

Structure solution and refinement. Following data reduction and the application of an absorption correction, direct methods (SHELXS 86[31]) yielded the position of the zinc atom and the carbon and boron atoms were located in subsequent difference syntheses. The hydrogen atoms were located in difference maps (SHELXL 93[32]); those on the carbon were refined using a riding model and those on the boron were refined with restraints such that all B–H and all Zn–H bond lengths were set to be equal, as were equivalent H–B–H angles. All hydrogen atoms were assigned isotropic thermal parameters equal to 1.2 times the equivalent thermal parameters of the atom to which they were joined (*i.e.* the carbon or boron). Refinement (against F^2) converged to a conventional R value of 0.072 [based on F and 462 data with $F > 4\sigma(F)$] and $wR_2 = 0.179$ (based on F^2 and all 502 data) with anisotropic thermal parameters on all non-hydrogen atoms (41 parameters). The final ΔF synthesis maximum and minimum were +0.66 and −0.63 e Å^{-3}, respectively, and the Flack absolute structure parameter refined to 0.2(2).

Complete atom coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

(*i*) Synthetic methods

The synthesis reported by Ridley[24] was found to afford the most convenient route to methylzinc tetrahydroborate inasmuch as it facilitated the growth from the vapour of crystals suitable for investigation by X-ray diffraction. Yields, based on reaction (1) and the amount of diborane taken, were typically 40%. This synthetic route is far from ideal, however, being awkward to perform on a scale sufficient to give significant amounts (100 mg or more) of the tetrahydroborate, and involving the manipulation of relatively large quantities of gaseous reagents. Attempts were therefore made to prepare methylzinc tetrahydroborate from the corresponding chloride and lithium tetrahydroborate, this being a commonly used route to tetrahydroborate derivatives, as exemplified by reaction (4).[11] In fact, though, this route was inferior, not only

$$\tfrac{1}{2}(H_2GaCl)_2 + LiBH_4 \longrightarrow H_2Ga(\mu\text{-}H)_2BH_2 + LiCl \quad (4)$$

in its yields (*ca.* 15%), but also in its ability to deliver good crystalline samples of methylzinc tetrahydroborate. Accordingly, the tetrahydroborate was usually prepared by Ridley's method.[24]

(*ii*) Physical properties

In agreement with the findings of Ridley[24] and Nibler and Cook,[25] methylzinc tetrahydroborate is a thermally fragile material decomposing *in vacuo* in all-glass apparatus at room temperature, typically over a period of several days. Continuous pumping at room temperature causes gradual disproportionation to Me_2Zn and $Zn(BH_4)_2$. The vapour pressure of the solid is *ca.* 0.5 Torr at room temperature, the thermal instability of the material ruling out further measurements at significantly higher temperatures. Consequently, it has so far proved impossible to produce a molecular flux of the compound sufficient for gas-phase electron-diffraction measurements.

(*a*) Proton and ^{11}B NMR spectra. The ^{1}H and ^{11}B NMR spectra of methylzinc tetrahydroborate in [^{2}H$_8$]toluene solution at various temperatures are illustrated in Fig. 1. The ^{1}H spectrum of the solution at room temperature shows a sharp singlet centred at δ_H −0.36 and a relatively broad 1:1:1:1 quartet centred at δ_H 0.82. The relative intensities of the signals (3:4) confirm that they are due to the methyl and tetrahydroborate protons, respectively. The quartet is the expected coupling pattern for a BH_4 group (^{11}B, $I = \tfrac{3}{2}$) in which there is rapid interchange of bridging and terminal hydrogen atoms.[8] The coupling constant $J(^{11}B-^{1}H)$ 83.2 Hz and the chemical shift of the BH_4 resonance correspond closely to those found for related compounds, *e.g.* Me_2GaBH_4[10] and $Al(BH_4)_3$.[15,33,34] The chemical shift of the methyl protons is also characteristic of a methyl group bound to zinc.[35] Cooling the sample caused the methyl resonance to remain unchanged but the BH_4 quartet progressively to collapse, giving a single, broad signal centred at δ_H 0.85 at −40 °C. This behaviour is characteristic of the protons of a molecular tetrahydroborate group;[8,36] the collapse of the multiplet structure of the BH_4 resonance can be rationalized in terms of correlation-time decoupling.[8] As is the case with most other molecular tetrahydroborates,[8] the ^{1}H NMR spectrum showed no sign of distinct resonances due to terminal and bridging BH_4 protons, even at −80 °C.

The ^{11}B NMR spectrum of methylzinc tetrahydroborate in [^{2}H$_8$]toluene solution at room temperature showed a 1:4:6:4:1 quintet centred at δ_B −39, a chemical shift in close agreement with that expected on the basis of the spectra of related compounds.[29] Collapse of the multiplet structure was observed to occur on cooling, for the reasons given above. There is no sign of any other ^{11}B signal even on cooling the solution to −90 °C.

Attempts to measure the molecular weight of methylzinc tetrahydroborate in solution using vapour-pressure-depression methods were precluded by the thermal sensitivity of the compound at room temperature and its sparing solubility in appropriate weakly co-ordinating solvents at significantly lower temperatures. The extent of association of methylzinc tetrahydroborate in solution therefore remains an open question.

(*b*) Infrared spectrum of solid methylzinc tetrahydroborate. The measured infrared spectra of annealed solid samples of $MeZnBH_4$, CD_3ZnBH_4 and $MeZnBD_4$ at 77 K were found to be very similar to those reported by Nibler and Cook,[25] who

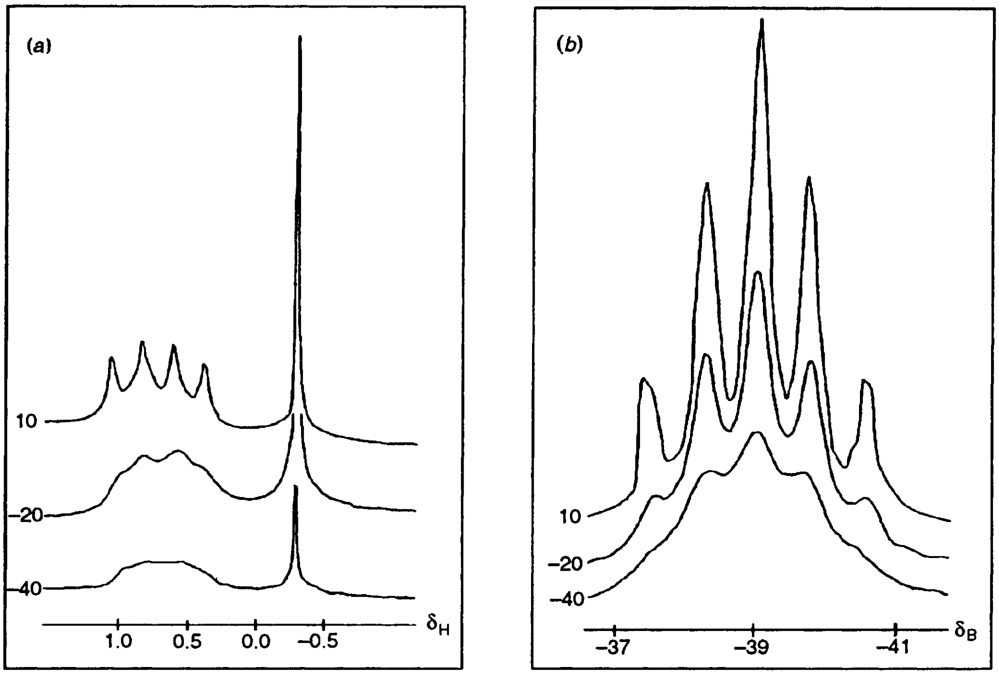


Fig. 1 Proton (*a*) and ^{11}B NMR (*b*) spectra of $MeZnBH_4$ in [$^2H_8$]toluene solution at −40, −20 and +10 °C

interpreted the results in terms of a structure containing more-or-less discrete $MeZn^+$ and BH_4^- ions with C_{3v} and D_{2d} symmetries, respectively. However, in the light of the crystal structure (see below) and of the existence of infrared bands at 443 and 1390 cm^{-1} assigned to the stretching vibrations of the Zn ••• B and bridging Zn–H units, respectively, the spectra are probably best interpreted in terms of a BH_4 group bridging two metal centres, *i.e.* in terms of $Zn(\mu\text{-}H)_2B(\mu\text{-}H)_2Zn$ fragments showing slight distortion from D_{2d} symmetry by bending of the Zn ••• B ••• Zn framework.

Matrices formed by co-condensing the vapour of methylzinc tetrahydroborate with an excess of argon or dinitrogen at *ca.* 20 K gave IR spectra consistent with the trapping of the monomer $MeZnBH_4$, with the structure $MeZn(\mu\text{-}H)_2BH_2$, together with what is believed to be an oligomer, probably $(MeZnBH_4)_2$. The vibrational properties and structures of these species will be discussed in a separate account.[37]

(*c*) **Mass spectrum.** This was measured by sampling the vapour above the solid at −30 and 0 °C. Mass peaks corresponding to the molecular ion of the monomer, $MeZnBH_4^+$, were observed, the intensity pattern of the peaks at m/z = 98, 96 and 94 matching the natural abundances of the zinc isotopes ^{68}Zn, ^{66}Zn and ^{64}Zn. Strong peaks were also observed at m/z values consistent with the species $MeZn^+$ and $ZnBH_4^+$, although the isotopic pattern is confused by the similar masses of the Me and BH_4 fragments. Mass peaks corresponding to the molecular ion of the dimer, $(MeZnBH_4)_2^+$ were also observed in both experiments. The intensity of peaks due to the dimer was observed to increase relative to those of the monomer as the temperature of the solid increased, implying that there is a greater proportion of the higher oligomer present in the vapour above solid $MeZnBH_4$ at higher temperature. This effect may well be due to the increased vapour pressure of $(MeZnBH_4)_n$ above the solid at the higher temperature, resulting in more frequent intermolecular collisions, as is thought to be the case with dimethylalane, $(Me_2AlH)_n$.[38]

(*iii*) Crystal structure of methylzinc tetrahydroborate at low temperature

The helical polymeric structure of $MeZnBH_4$ is illustrated in Fig. 2, while the view along the axis of the helix is represented in Fig. 3. Bond distances and angles are given in Table 1, fractional atomic coordinates in Table 2.

The structural results show that the solid consists of helical polymers in which successive methylzinc units are linked by BH_4^- groups exhibiting bidentate ligation with respect to both metal atoms. In this respect, the structure closely resembles that of beryllium bis(tetrahydroborate), which has been shown to consist of $Be(\mu\text{-}H)_2BH_2$ units bridged by BH_4 ligands.[17] In the beryllium compound the interaction of the metal with six hydrogen atoms leads to trigonal-prismatic co-ordination of the metal. In the case of methylzinc tetrahydroborate, however, the zinc atom is clearly only five-co-ordinated, the ligands adopting a distorted square-pyramidal geometry about the metal atom which is situated *ca.* 0.8 Å above the best plane through the four adjacent hydrogen atoms furnished by the BH_4 groups. It is interesting that the dimensions determined for the $Zn(\mu\text{-}H)_2B$ moiety are very similar to those reported recently for the compound $Zn(H_2BH_2)Cl(tmen)$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), in which the zinc atom is also five-co-ordinate.[39] In particular, the Zn ••• B and Zn–H distances and the H–Zn–H angles are very similar. In the chloro compound the Lewis basicity of the bidentate ligand tmen may be expected to promote some degree of separation of $ZnCl(tmen)^+$ and BH_4^- units; the similarity in the dimensions of the $Zn(\mu\text{-}H)_2B$ units of the two compounds provides evidence of some degree of charge separation in solid methylzinc tetrahydroborate.

Further comparison with the structure of solid beryllium bis(tetrahydroborate)[17] shows that, whereas the beryllium compound is disposed around a 4_1 axis, solid methylzinc tetrahydroborate spirals along a 3_1 axis. This difference reflects the contrasting co-ordination geometries at the metal centres and, in particular, the B–M–B (M = Zn or Be) angles within the helical chain. The B–M–B angle is 98.6° in methylzinc tetrahydroborate compared with 111.7° in beryllium bis(tetrahydroborate), a difference which may in part depend upon the greater separation of the zinc and boron atoms. This facilitates closure of the B–M–B angle while keeping the B ••• B distance, and hence electrostatic repulsion, between adjacent BH_4 ligands approximately constant [adjacent B ••• B distances are 3.49 Å in $MeZnBH_4$ and 3.29 Å in $Be(BH_4)_2$[17]].

The structures of both $MeZnBH_4$ and $Be(BH_4)_2$ exhibit some

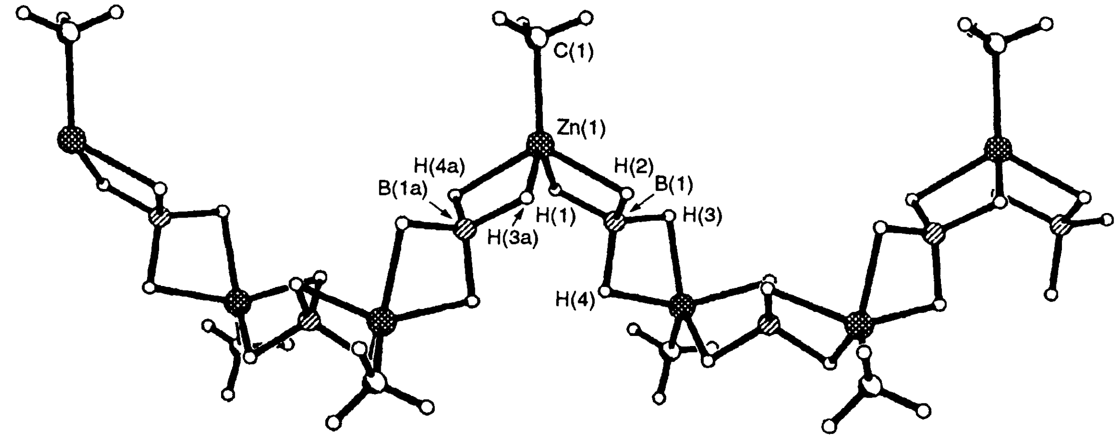


Fig. 2 Helical polymeric structure of solid methylzinc tetrahydroborate at 150 K as determined by X-ray diffraction

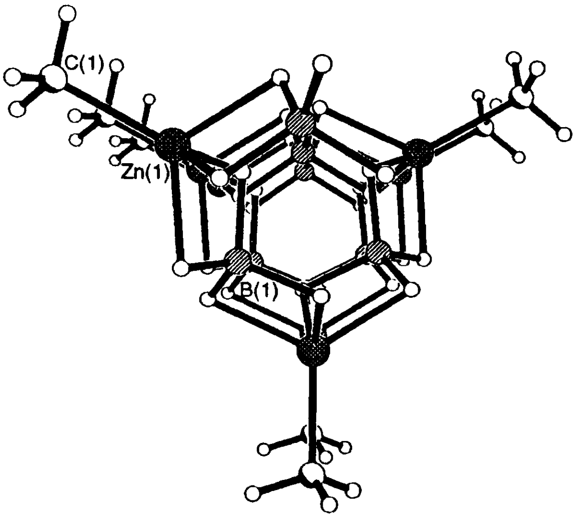


Fig. 3 Structure of solid methylzinc tetrahydroborate at 150 K as viewed along the axis of the helix

Table 1 Bond distances (Å) and angles (°) for crystalline $MeZnBH_4$ at 150 K*

Zn(1)–C(1)	1.94(2)	B(1)–Zn(1″)	2.32(2)
Zn(1)–B(1)	2.30(2)	B(1)–H(1)	1.33(4)
Zn(1)–B(1′)	2.32(2)	B(1)–H(2)	1.33(4)
Zn(1)–H(1)	1.82(5)	B(1)–H(3)	1.32(4)
Zn(1)–H(2)	1.81(5)	B(1)–H(4)	1.36(5)
C(1)–Zn(1)–B(1)	129.8(7)	Zn(1)–B(1)–H(2)	52(2)
C(1)–Zn(1)–B(1′)	131.5(7)	Zn(1″)–B(1)–H(2)	125(3)
B(1)–Zn(1)–B(1′)	98.6(7)	H(1)–B(1)–H(2)	103(3)
C(1)–Zn(1)–H(1)	117(3)	Zn(1)–B(1)–H(3)	137(3)
B(1)–Zn(1)–H(1)	35.2(14)	Zn(1″)–B(1)–H(3)	51(2)
B(1′)–Zn(1)–H(1)	101(4)	H(1)–B(1)–H(3)	115(4)
C(1)–Zn(1)–H(2)	122(4)	H(2)–B(1)–H(3)	114(4)
B(1)–Zn(1)–H(2)	35.3(14)	Zn(1)–B(1)–H(4)	121(2)
B(1′)–Zn(1)–H(2)	98(4)	Zn(1″)–B(1)–H(4)	51(2)
H(1)–Zn(1)–H(2)	70(2)	H(1)–B(1)–H(4)	111(4)
Zn(1)–B(1)–Zn(1″)	171.9(3)	H(2)–B(1)–H(4)	112(4)
Zn(1)–B(1)–H(1)	52(2)	H(3)–B(1)–H(4)	102(3)
Zn(1″)–B(1)–H(1)	132(2)		

* Symmetry operations: single prime $-y + \frac{4}{3}, x - y - \frac{1}{3}, z - \frac{1}{3}$; double prime $-x + y + \frac{5}{3}, -x + \frac{4}{3}, z + \frac{1}{3}$.

Table 2 Fractional atomic coordinates for $MeZnBH_4$

Atom	*x*	*y*	*z*
Zn(1)	0.9444(1)	0.1807(1)	0.9337*
C(1)	0.9972(11)	0.0404(11)	0.9247(24)
B(1)	0.9122(14)	0.2751(12)	1.1052(24)
H(1a)	0.921(6)	0.024(1)	0.843(9)
H(1b)	0.818(2)	0.010(1)	0.897(13)
H(1c)	0.894(7)	0.016(1)	1.029(4)
H(1)	0.863(5)	0.228(7)	0.975(9)
H(2)	0.978(6)	0.246(7)	1.122(8)
H(3)	0.858(6)	0.261(4)	1.234(9)
H(4)	0.955(7)	0.373(4)	1.085(9)

* The origin was fixed by fixing this parameter.

degree of charge separation, $RM^+BH_4^-$ (M = Be, R = BH_4; M = Zn, R = Me) but both compounds are volatile, giving rise to more covalently bound species in the vapour phase.[40] On the basis of infrared measurements and of comparisons with the spectra of ionic tetrahydroborates, Nibler and Cook[25] suggested that solid methylzinc tetrahydroborate was based around a linear ZnBZn framework and consequently around a BH_4^- ion effectively possessing D_{2d} symmetry. In fact, the crystal structure shows a Zn–B–Zn angle of 171.9° and, although it does suggest loss of all symmetry elements from the BH_4^- ion [as is indeed also the case for $Be(BH_4)_2$[17]], the observed distortion from D_{2d} symmetry is small. Nibler and Cook[25] further asserted that the BH_4^- ion is less strongly coupled to the metal in $MeZnBH_4$ than in $Be(BH_4)_2$. Comparison of the two crystal structures, however, reveals some evidence to the contrary. Thus, we find that the B–H bonds within the helical chain are significantly longer in $MeZnBH_4$ [typically 1.33(4) Å, compared with 1.10(4) Å in $Be(BH_4)_2$[17]], indicating that the interaction of the metal centre with the bridging hydrogen atoms is in fact somewhat stronger in the zinc compound. Enhanced interaction with the metal might also be expected to cause greater distortion of the H–B–H angles from the tetrahedral value, manifesting the existence of two distinct bidentate BH_2 units. In fact, although these angles do appear to show greater distortion in $MeZnBH_4$ than in $Be(BH_4)_2$, the difference between the values is exceeded by the relatively large uncertainties in the measurements.

Polymeric structures incorporating bridging ligands are relatively common in zinc chemistry (*e.g.* ZnH_2[41]), five-co-ordinated zinc centres are encountered less often. Most examples of either square-pyramidal or trigonal-bipyramidal co-ordination, including the newly reported $Zn(H_2BH_2)Cl(tmen)$,[39] are complexes involving polydentate ligands with O, S, Se or N donor atoms.[42] Among authenticated simple hydride derivatives of zinc, though, methylzinc tetrahydroborate is certainly a rare example of this mode of co-ordination, another example being the very recently reported $[(MeZn)_2B_3H_7]_2$.[43] The crystal structure of this compound contains two methylzinc units bridged not by BH_4 groups but by two novel B_3H_7ZnMe ligands to give a centrosymmetric dimeric cluster.[43] The geometry of the Zn(1) centre in $[(MeZn)_2B_3H_7]_2$ resembles closely that in $MeZnBH_4$ in that both feature five-co-ordinated zinc with Me and H ligands adopting a distorted square-pyramidal geometry about the metal centre. In each case the methylzinc unit is linked to the borane ligand *via* Zn–H–B bonds and this is reflected in the similar Zn $\cdots$ B distances {2.30 and 2.32 Å in $MeZnBH_4$; 2.41 and 2.45 Å in $[(MeZn)_2B_3H_7]_2$}.[43] Presumably the fact that $MeZnBH_4$ is polymeric but $[(MeZn)_2B_3H_7]_2$ is a dimer reflects the different constraints imposed by the two ligands in order for the zinc centres to achieve maximum co-ordination. Each BH_4 ligand must bond in bidentate fashion to each adjacent zinc atom to achieve five-co-ordination, implying an approximately linear Zn $\cdots$ B $\cdots$ Zn skeleton and hence a polymeric structure. In $[(MeZn)_2B_3H_7]_2$ five-co-ordination is achieved by using all four hydrogens of the basal $H_2B–BH_2$ unit of the B_3H_7ZnMe ligand which allows folding of the skeleton and a dimeric structure.

(*iv*) Chemical properties

Some of the chemical properties of methylzinc tetrahydroborate have been explored, with the results summarized in Scheme 1. Our survey has taken in not only the decomposition of the compound at or near ambient temperatures, but also its behaviour with respect to each of four selected Lewis bases (NH_3, SMe_2, PPh_3 and CO). The reaction pathways thus revealed will now be treated in turn.

(*a*) Thermal decomposition. As noted already, continuous pumping at room temperature causes methylzinc tetrahydroborate gradually to disproportionate with the formation of volatile dimethylzinc and involatile zinc bis(tetrahydroborate), as in equation (5). Heating the compound in a sealed ampoule to

$$2MeZnBH_4 \longrightarrow Me_2Zn + Zn(BH_4)_2 \qquad (5)$$

temperatures approaching 100 °C causes the solid to turn grey, with the evolution of dimethyldiborane and hydrogen. Under these conditions the decomposition proceeds according to reaction (6).

$$2MeZnBH_4 \longrightarrow (MeBH_2)_2 + 2H_2 + 2Zn \qquad (6)$$

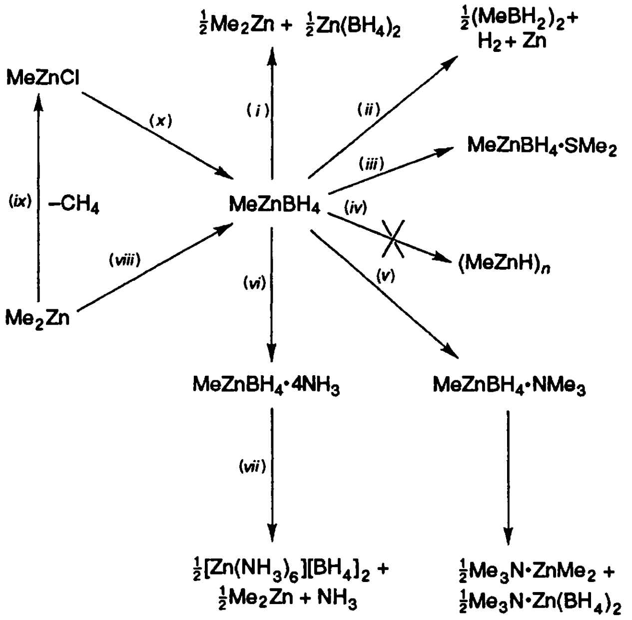
(*b*) Reaction with ammonia. The reaction of methylzinc tetrahydroborate with ammonia was of interest principally for two reasons: (*a*) as a route to a more thermally robust species which might provide a reliable method of analysis, and (*b*) for the comparison it affords with the reaction with trimethylamine reported by Ridley[24] to proceed as follows in equations (7) and (8).

$$MeZnBH_4 + NMe_3 \longrightarrow MeZnBH_4{\cdot}NMe_3 \qquad (7)$$

$$2MeZnBH_4{\cdot}NMe_3 \longrightarrow Me_3N{\cdot}ZnMe_2 + Me_3N{\cdot}Zn(BH_4)_2 \qquad (8)$$

Methylzinc tetrahydroborate reacts with ammonia at −78 °C to give an adduct $MeZnBH_4{\cdot}4NH_3$ which decomposes on warming to 0 °C. That the infrared spectrum of this adduct contains bands associated with the $MeZn^+$ unit,[25] with the BH_4^- anion (at 2332, 2245, 1244 and 1101 cm^{-1}),[8] and with co-ordinated ammonia[44,45] suggests the formulation $[MeZn(NH_3)_4]^+[BH_4]^-$. Other molecular tetrahydroborates, such as $Al(BH_4)_3$,[46,47] H_2GaBH_4,[11] Me_2GaBH_4[10] and even B_2H_6 itself,[48] are known to react with an excess of ammonia in a similar fashion to yield analogous adducts in which the BH_4^- ion has been displaced from the co-ordination sphere of the metal.

The thermal decomposition of $MeZnBH_4{\cdot}4NH_3$ at 0 °C proceeds with the evolution of 1 mol of ammonia and half a mol of dimethylzinc, leaving an involatile, white solid with the composition $ZnN_6B_2H_{26}$ on the basis of elemental analysis. Comparison of the IR spectrum of the solid residue with those of ammines of the type $[Zn(NH_3)_6]X_2$ (X = Cl, Br or I)[44,49,50] and of ionic tetrahydroborates[8] implies the presence of more-or-less discrete $[Zn(NH_3)_6]^{2+}$ and BH_4^- ions.



Scheme 1 Chemical properties of methylzinc tetrahydroborate. (*i*) 290 K, continuous pumping; (*ii*) heat, 373 K; (*iii*) 250 K, Me_2S; (*iv*) CO or PPh_3; (*v*) NMe_3;[24] (*vi*) NH_3, 195 K; (*vii*) warm to 273 K; (*viii*) B_2H_6, 290 K; (*ix*) HCl; (*x*) $LiBH_4$, 290 K

The reaction with ammonia is therefore probably best written as in equations (9) and (10) and mirrors both the thermal

$$MeZnBH_4 + 4NH_3 \longrightarrow [MeZn(NH_3)_4]^+[BH_4]^- \qquad (9)$$

$$2[MeZn(NH_3)_4]^+[BH_4]^- \longrightarrow ZnMe_2 + 2NH_3 + [Zn(NH_3)_6]^{2+}2[BH_4]^- \qquad (10)$$

decomposition at room temperature and the reaction with trimethylamine[24] in that it effectively brings about disproportionation into dimethylzinc and zinc bis(tetrahydroborate). The reaction also provides a reliable method of analysing methylzinc tetrahydroborate, other methods being thwarted by the thermal fragility of the parent compound. Chemical analysis of the more robust $[Zn(NH_3)_6][BH_4]_2$, together with tensimetric measurements of the amount of dimethylzinc evolved and the net amount of ammonia taken up, yielded the following results: Found C, 13.20; H, 6.65; B, 11.00; Zn, 69.05. Calc. for $MeZnBH_4$: C, 12.60; H, 7.40; B, 11.35; Zn, 68.65%. The indirect nature of the analysis, incorporating several stages and various measurements, and the presence of a small quantity of occluded dimethylzinc in the $[Zn(NH_3)_6][BH_4]_2$ probably account for the small discrepancies between the measured and calculated values.

(*c*) Reaction with dimethyl sulfide. The reaction of $MeZnBH_4$ with an excess of dimethyl sulfide at −23 °C proceeds in accordance with equation (11) yielding a viscous, slightly

$$MeZnBH_4 + SMe_2 \longrightarrow MeZnBH_4{\cdot}SMe_2 \qquad (11)$$

volatile liquid which decomposes upon prolonged pumping at room temperature with the evolution of free dimethyl sulfide. The ^1H NMR spectrum of a solution of the adduct in $[^2H_8]$toluene shows singlets at δ_H 1.50 and −0.39 and a quartet centred at δ_H 0.9. These are assigned to the Me_2S,

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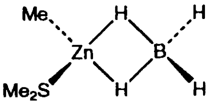
† The measured ^1H chemical shift of dimethyl sulfide (*ca.* 1 mol dm^{-3}) in $[^2H_8]$toluene solution at room temperature was found to be δ 1.73.



1

MeZn and BH_4 protons respectively. Integration of the signals proved difficult because of overlapping of the Me_2S singlet and one component of the BH_4 quartet. The ^{11}B NMR spectrum shows a single resonance, a quintet centred at δ_B −47.8 [$J(^{11}B-^{1}H)$ = 86.0 Hz]. Evidence that the complex $MeZnBH_4\cdot SMe_2$ remains more-or-less intact in solution is provided by the fact that the observed signals are shifted from those expected for 'free' SMe_2† and $MeZnBH_4$.

The infrared spectrum of $MeZnBH_4\cdot SMe_2$ isolated in solid dinitrogen at 14 K exhibits several features of note. Clearly in evidence are bands associated with co-ordinated SMe_2,[51] as well as bands attributable to the $MeZnBH_4$ fragment. Although the actual positions of the latter show slight shifts from those observed for the uncomplexed monomeric molecule, the pattern remains similar. In particular, the region of the spectrum associated with the stretching motions of B–H bonds resembles closely that of 'free' monomeric $MeZnBH_4$, and is therefore highly suggestive of bidentate ligation of the BH_4 group.

The infrared spectrum of an annealed solid film of $MeZnBH_4\cdot SMe_2$ at 14 K shows somewhat broader bands but with wavenumbers similar to those observed for the matrix-isolated species. In particular, distinct bands attributable to the stretching fundamentals of terminal and bridging B–H bonds persist in the spectrum of the solid, in stark contrast to the behaviour of uncomplexed $MeZnBH_4$. It seems likely therefore that $MeZnBH_4\cdot SMe_2$ retains the molecular structure **1** in the solid phase in contrast to the polymeric nature of the solid parent compound.

(*d*) Studies with triphenylphosphine and CO. Both PPh_3 and CO are reported to react with metal tetrahydroborate derivatives to yield the corresponding metal hydride and the adduct $L\cdot BH_3$ (L = PPh_3 or CO),[1a,52] *e.g.* equations (12) and (13). Accordingly, the reactions of PPh_3 and CO (L) with

$$HGa(BH_4)_2 + CO \longrightarrow H_2GaBH_4 + OC\cdot BH_3 \quad (12)$$

$$Be(BH_4)_2 + 2PPh_3 \longrightarrow BeH_2 + 2(Ph_3P\cdot BH_3) \quad (13)$$

$$MeZnBH_4 + L \longrightarrow \tfrac{1}{n}(MeZnH)_n + L\cdot BH_3 \quad (14)$$

$MeZnBH_4$ were investigated as potential routes to $(MeZnH)_n$ *via* reaction (14). Even in protracted experiments, however, there was no sign of $OC\cdot BH_3$ and only traces of $Ph_3P\cdot BH_3$ were detected. Attempts to carry out the reactions at higher temperatures were frustrated by the thermal fragility of $MeZnBH_4$ itself.

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