The Methylzinc Hydroborate Derivative [(MeZn)2B3H7]2: Synthesis, Crystal Structure and Vibrational Spectra of an Unprecedented Cluster Compound

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The bis(methylzinc) derivative of triborane(9), prepared by the gas-phase reaction of B_4H_{10} with Me_2Zn at ambient temperature, is a dimer [(MeZn)2B3H7]2 with an unprecedented structure featuring two distinct zinc environments; two B_3H_7ZnMe ligands, formally derived from B_3H_8 by replacement of a μ_2-H by a μ_2-ZnMe unit, each function in a bis(bidentate) manner linking together two other MeZn centres through pairs of Zn–H–B bridges.

Despite their synthetic potential, very few hydroborate complexes of zinc have been reported,[1-5] and of these only [MeZnBH4][6] and [(Ph3PMe)2Zn(B10H12)2][1] have been structurally characterised. Here we report the synthesis and structural characterisation of an unexpected and novel cluster compound [(MeZn)2B3H7]2.

The reaction between B_4H_{10} and a threefold excess of Me_2Zn in the gas phase at ambient temperatures affords, not the expected product [MeZnB3H8], but colourless acicular crystals of [(MeZn)2B3H7]2 in yields of ca. 10%. This compound is involatile, extremely air- and moisture-sensitive, and decomposes in vacuo over a period of ca. 48 h at room temp. Heating to 150 °C to ensure complete decomposition affords a solid residue containing only zinc and boron, hydrogen gas and a mixture of methylboranes, BMe3 and [MeBH2]2. Single crystals were loaded into capillaries fused directly to the reaction vessel and held at 150 K for the collection of X-ray diffraction data.† Further characterisation of the compound was achieved by measurement of its IR, FT-Raman and NMR spectra and by elemental analysis.

The structure of [(MeZn)2B3H7]2, 1, is shown in Fig. 1. Although the nature of the heavy atom skeleton is well defined by X-ray diffraction, the positions of hydrogen atoms are less well determined. However, comparison with similar structures and examination of the IR, Raman and NMR spectra of the compound provide strong evidence that the hydrogen locations are as indicated.

The crystal structure of 1 consists of discrete centrosymmetric Me4Zn4B6H14 clusters in which two novel B3H7ZnMe units are linked through hydride bridges about a central MeZn···ZnMe vector [3.014(3) Å], in an unusual example of a molecule containing two chemically distinct zinc environments. Zn(1) is five-coordinated, being bound to a terminal methyl group and four bridging hydrogen atoms (supplied by the

Fig. 1 The molecular structure of 1. Relevant bond lengths (Å) and angles (°) are: B(1)–B(2) 1.76(2), B(1)–B(3) 1.83(2), B(2)–B(3) 1.76(2), Zn(1)–B(2) 2.41(2), Zn(1)–B(3) 2.45(2), Zn(2)–B(1) 2.20(2), Zn(2)–B(2) 2.15(2), Zn(1)···Zn(1A) 3.014(3); B(2)–B(1)–B(3) 58(9), B(1)–B(2)–B(3) 62.7(9), B(1)–B(3)–B(2) 58.8(9), B(1)–Zn(2)–B(2) 47.8(7). 'A' indicates the symmetry transformation −x, −y, −z + 2.

B3H7ZnMe units) forming a distorted square pyramid. A similar motif occurs in the solid state structure of [MeZnBH4],[6] while the 'side-on' bridging function of the B3-units is reminiscent of the structure of [Mn2(CO)6(μ-Br)(B3H8)].[7] The B3H7ZnMe unit can be conceived as being derived from the well-known $B_3H_8^-$ anion by replacement of one bridging hydrogen by ZnMe. Zn(2) is thus three-coordinated, being attached to a terminal methyl group and, in an especially remarkable feature, to two boron atoms [B(1) and B(2)] via a three-centre two-electron bond. The Zn(2)–B(1,2) bond lengths [2.20(2) and 2.15(2) Å] are significantly shorter than the Zn(1)···B(2,3) distances [2.41(2) and 2.45(2) Å], but very similar to those observed in the cluster [Zn(B10H12)2]²⁻ [2.197(10) and 2.209(10) Å],[1] in which the zinc is bound directly to four boron atoms. Consistently, the BZnB bond angle in 1 [47.8(7)°] is also similar to those in [Zn(B10H12)2]²⁻ [42.7(4)°][1] and [B10H12TlMe2]⁻ [37.3(6)°],[8] as are the angles subtended at the boron atoms. The B–B bond lengths within the B3-unit adopt usual values.[7,9]

The FTIR and FT-Raman spectra of solid 1 corroborate the crystal structure which displays a centre of inversion, so that no vibrational transitions are expected to be active in both IR absorption and Raman scattering. This appears indeed to be the case. The vibrational spectra also provide persuasive evidence for the existence of a BH2 group. Thus, the IR spectrum shows two bands (at 2465 and 2415 cm⁻¹) in the region characteristic of $v(B–H_t)$ fundamentals (t = terminal),[10] with wavenumbers and splitting similar to the bands attributed to the corresponding modes of the apical BH2 group in solid [CsB3H8];[11] bands attributable to the twisting, deformation, rocking and wagging modes of a BH2 group[12] can also be found at 1140, 1090, 976 and 778 cm⁻¹, respectively. These features endorse the existence of two terminal hydrogen atoms attached to B(1) and make it unlikely that either hydrogen is involved in bonding to Zn(2) via a Zn–H–B linkage. Bands attributable to the stretching of bridging B–H bonds in B–H–Zn (2257 cm⁻¹) and B–H–B units (1919 cm⁻¹) find counterparts in the spectra of solid [MeZnBH4] (2257 cm⁻¹)² and [(H)(OC)3FeB3H8] (1915 cm⁻¹).[13] Prominent in the Raman spectrum are two equally intense bands at 563 and 539 cm⁻¹ arising from v(Zn–C) modes {cf. 557 cm⁻¹ for solid |MeZnBH4|² and 558 cm⁻¹ (mean of v_s and v_{as}) for [Me2Zn][14]}. This is consistent with the presence of two distinct MeZn environments in 1. Intense scattering at 226 cm⁻¹ probably originates in a Zn–B stretching motion involving the ZnB2 ring, in keeping with the vibrational assignments proposed for compounds of the type [(Me4N)2M(B10H12)2] (M = Zn, Cd or Hg).[15]

The ¹¹B NMR spectrum of 1 in [²H8]toluene solution at low temperatures indicates the presence of more than one species [possibly involving different states of aggregation of (MeZn)2B3H7, an interpretation which invites further investigation]. With the solution at 20 °C, however, the spectrum shows three distinct resonances of equal intensity at δ_B −25.5, −34.1 and −55.0, the first two apparently being broad singlets and the third a 1 : 2 : 1 triplet. These observations are consistent with a species along the lines illustrated in Fig. 1 incorporating three distinct boron atoms, one bound to two equivalent
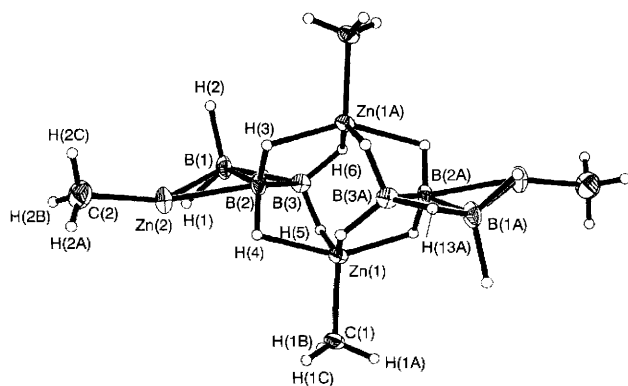
terminal hydrogen atoms and the other two bearing no such atoms. Coupling to bridging hydrogens appears not to be resolved, the linewidths typically being large (*ca.* 200 Hz) in comparison with expected coupling constants for bridging hydrogens.[16] The ^{1}H NMR spectrum of the solution at temperatures in the range +20 to −60 °C shows three broad signals attributable to protons bound to boron at δ_H (i) 0.45 (extremely broad resonance, linewidth *ca.* 200 Hz), (ii) −1.24 [1 : 1 : 1 : 1 quartet] and (iii) −2.41, with intensities in the ratio 4 : 2 : 1. These are assigned, respectively, (i) to the bridging protons H(3), H(4), H(5) and H(6), (ii) to the protons of the BH$_2$ group [H(1) and H(2)], and (iii) to the bridging proton of the B–H–B group [H(13)].

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Footnotes

† Crystals of [(MeZn)$_2$B$_3$H$_7$]$_2$ were obtained by the reaction of B$_4$H$_{10}$ (5.0 mmol) with a threefold excess of Me$_2$Zn in a 1 1 bulb at room temp. over a period of 16 h. Volatile co-products were BMe$_3$ and CH$_4$ (*ca.* 0.5 mmol of each). Satisfactory elemental analyses were obtained by assaying the products of thermal decomposition and of the reaction with concentrated HNO$_3$.

Crystal data: C$_4$H$_{26}$B$_6$Zn$_4$, M = 400.59, monoclinic, $P2_1/c$, a = 10.0382(12), b = 7.8137(11), c = 11.0764(16) Å, β = 11.923(9)°, U = 806.0(3) Å^3 [from 2θ values of 60 reflections measured at ±ω (24° ≤ 2θ ≤ 34°), λ = 0.71073 Å], Z = 2, D_c = 1.651 g cm^{-3}, T = 150 K, colourless needle, μ = 5.84 mm^{-1}.

Data collection and processing. Stoe Stadi-4 four circle diffractometer fitted with an Oxford Cryosystems low-temperature device,[17] graphite-monochromated Mo-Kα radiation, with ω–θ scans, ω-halfwidth (1.5 + 0.35tan θ)°, −11 ≤ h ≤ 10, −8 ≤ k ≤ 8, 0 ≤ l ≤ 11. The structure was solved for all non-H atoms by direct methods,[18] and refined against F^2 with full-matrix least-squares analysis.[19] The hydrogen atoms on the methyl groups were located in a difference synthesis which described the locus of the possible positions of these atoms and subsequently refined using a riding model, with U_{iso}(H) = 1.5U_{eq}(C). Four of the remaining hydrogen atoms

[H(1), H(2), H(5) and H(13)] were located in a difference synthesis performed after several cycles of least squares weighted towards the high angle data; the remaining hydrogen positions were inferred from this map. These hydrogen atoms were then refined within variable-metric rigid groups with the restraint that chemically equivalent B–H and Zn–H distances were equal, U_{iso}(H) = 1.2U_{eq}(B). The refinement converged to a conventional R value of 0.0623 [based on F and 623 data with F > 4σ(F)] and wR_2 of 0.1516 (based on F^2 and all 1069 data) for 70 refined parameters. The final difference synthesis maximum and minimum were 1.06 and −0.62 e Å^{-3}, respectively.

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