Structure and Bonding of the Lithium Tetrahydroborate–Tetramethylethylenediamine Adduct $(TMEDA{\cdot}LiBH_4)_2$, a Centrosymmetric Dimer containing Doubly and Triply Bridging Hydrogen Atoms

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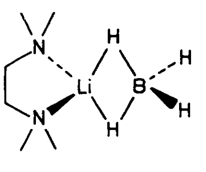
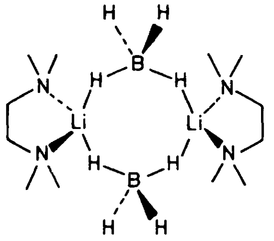
The title compound, the first alkali metal tetrahydroborate complex to be structurally characterised, has been shown by an *X*-ray study to be dimeric in the crystal, with each μ_2,η^3-BH_4 group bonding to two metal atoms through one μ_2-hydrogen atom apiece and also through one μ_3-hydrogen atom; MO calculations at the 6-31G level on unsolvated $LiBH_4$ and the model adducts $(H_2O)_n{\cdot}LiBH_4$ (n = 1 or 2) and their dimers, with η^2- and η^3-BH_4 geometries, show how their stabilities reflect the number of Li - - - H contacts, whilst illustrating the inadequacies of LiHB and Li_2HB 3- and 4-centre bond schemes for such compounds.

Although alkali metal tetrahydroborates MBH_4 are widely used as reducing or hydroborating agents in inorganic, organic, and organometallic chemistry,[1] and Lewis bases are known to have a significant influence on their reactivity, surprisingly little structural work has been done to probe the metal–hydroborate interactions that presumably affect their reactions.[1,2] Such interactions are expected to be most marked in the case of lithium tetrahydroborate, whose neglect is especially surprising in view of the structural attention other lithium systems have commanded recently.[3] The structures of two lithium hydroborates, $LiBH_2(mesityl)_2{\cdot}2MeOCH_2CH_2OMe$[4] (**1**) and $LiBH_3C(SiMe_2Ph)_3{\cdot}3THF$[5] (**2**) (THF =



(I)



(II)

Table 1. Calculated relative electronic energies (kcal mol^{-1})[a] of $LiBH_4$ and its derivatives.

	$E(\eta^3-\eta^2)$[b]	ΔE (Dimerisation)[c]	ΔE (Solvation)[d]
$LiBH_4$	−3.5	-	-
$H_2O{\cdot}LiBH_4$	−3.2	-	−30.9
$(H_2O)_2{\cdot}LiBH_4$	−3.1	-	−54.2
$(LiBH_4)_2$	−10.6	−37.8	-
$(H_2O{\cdot}LiBH_4)_2$	−5.8	−31.7	−55.6
$[(H_2O)_2{\cdot}LiBH_4]_2$	−3.3	−20.1	−90.7

[a] 1 cal = 4.184 J. [b] Difference in energy between η^3- and η^2-BH_4 geometries. [c] Difference in energy between dimer and two monomers. [d] Difference in energy between adduct$(H_2O)_n{\cdot}$ $LiBH_4$ (n = 1 or 2) and $LiBH_4$ + 1 or 2 H_2O.

tetrahydrofuran) have been determined recently, but are not expected to be typical because of substituent bulk effects. We chose the title compound, TMEDA·$LiBH_4$ (**3**) (TMEDA = tetramethylethylenediamine) for structural study as a representative (indeed, commercially available) complex L_2LiBH_4, where L_2 is a bidentate Lewis base. Compound (**3**) is formed when $LiBH_4$ is treated with an excess of TMEDA, and crystallises from toluene–TMEDA as colourless hygroscopic plates whose high solubility in hydrocarbon as well as other solvents contributes significantly to its scope as a reagent. The chelating base TMEDA was expected to restrict to two AO's per metal atom the number of metal orbitals available for metal–hydroborate bonding. Possible structures envisaged were (I) and (II), each involving the metal in two 2-centre Li–N bonds and two 3-centre Li–H–B bonds.

An X-ray crystallographic study of (**3**) showed neither (I) nor (II) to be correct, but established the presence of the centrosymmetric dimeric molecules shown in Figure 1.† Remarkably, the BH_4 residues bond through *three* of their four hydrogen atoms, two μ_2, one μ_3, and the metal atoms are *six*-co-ordinate, not four-co-ordinate as expected in (I) or (II). Such a bonding mode for BH_4^- ligands has to our knowledge only one precedent in the cobalt complex $[Co(BH_4)(Ph_2PC_5H_{10}PPh_2)]_2$ (**4**)[6] where its presence was attributed to the effect of the diphosphine ligands, and the electron-counting implications were obscured by uncertainties about what metal–metal interactions were involved. Borohydride anions BH_4^- have been considered[7] as sources of 2, 4, or 6 electrons when they co-ordinate to metal atoms through one, two, or three hydrogen atoms, respectively, as in $MeC(CH_2PPh_2)_3Cu(\mu_2\text{-}H)BH_3$,[8] $(Ph_3P)_2Cu(\mu_2H)_2BH_2$,[9] or $Zr[(\mu_2\text{-}H)_3BH]_4$.[10] However, the structures of compounds (**1**)—(**4**) show that such valence shell electron counts may be misleading, apparently requiring the metal atoms to accommodate more than the expected 8 (for Li) or 18 (for Co) electrons.

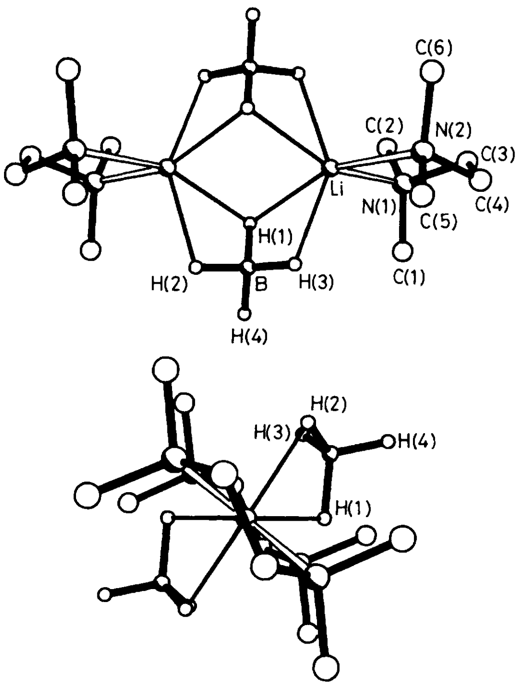


Figure 1. Two views of the molecular structure of (**3**). Key dimensions: Li–B 2.467(5), Li–B′ 2.461(6), Li–Li′ 3.089(9), Li–N(1) 2.125(6), Li–N(2) 2.115(6), Li–H(1) 2.07(3), Li–H(1′) 2.12(3), Li–H(2′) 2.06(4), Li–H(3) 2.02(3), B–H(1) 1.19(4), B–H(2) 1.17(4), B–H(3) 1.07(4), B–H(4) 1.06(4) Å; the prime denotes an atom related by the inversion centre.

To probe the bonding in (**3**) we have carried out MO calculations[11,12] at the 6-31G level on the monomers and dimers of $LiBH_4$, $H_2O{\cdot}LiBH_4$, and $(H_2O)_2{\cdot}LiBH_4$ (where H_2O molecules were mimicking the solvation effect of TMEDA). For each of the six model systems we optimised its structure with both η^2 and η^3 BH_4 geometries present (previously[13] only monomeric, unsolvated $LiBH_4$ had been subjected to a theoretical study which found that the η^3 BH_4 geometry that maximises the number of B - - - H - - - Li links provided the most stable structure). Our calculations show that the η^3 BH_4 structures are preferred in *all* cases, monomers *and* dimers, and that the dimeric forms are energetically favourable (see Table 1). Repeating the geometry optimisation procedure on for example η^3-$(LiBH_4)_2$ and employing only a 1s orbital in the lithium basis set had little effect on the length of the B–H and Li- - -H bonds which differed at most by 0.003 and 0.055 Å, respectively, when compared to the corresponding full basis set optimised distances; this underlines the predominantly ionic nature of the bonding. The Mulliken charge distribution in $[(H_2O)_2{\cdot}LiBH_4]_2$, our model for $(TMEDA{\cdot}LiBH_4)_2$, gives a total charge on the BH_4 group of −0.64 e with the bridging hydrogens having charges of −0.11 e (μ_3) and −0.13 e (μ_2) while the terminal hydrogen carries 0.08 excess electrons; the water

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† *Crystal data* for (**3**): $C_{12}H_{40}B_2Li_2N_4$, triclinic, space group $P\bar{1}$, dimer, a = 8.2201(8), b = 8.3090(6), c = 8.7538(10) Å, α = 89.583(7), β = 88.338(6), γ = 64.130(6)°, U = 537.74 Å^3, Z = 1 (dimer), D_c = 0.852 g cm^{-3}, $F(000)$ = 156, Cu-K_α radiation, λ = 1.54184 Å, μ = 0.33 mm^{-1}. The structure was solved by direct methods and refined by weighted blocked-cascade least-squares [$w^{-1} = \sigma^2(F) + 0.00157F^2$]; anisotropic thermal parameters were used for all non-hydrogen atoms, isotropic for the freely refined BH_4 hydrogen atoms; other hydrogen atoms were constrained, with C–H 0.96 Å, H–C–H 109.5°, $U(H) = 1.2U_{eq}(C)$. R = 0.089, R_w = 0.124 for 1111 unique reflections with $F > 4\sigma(F)$ and 119 parameters. 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.

molecules donate 0.13 e to lithium resulting in an overall charge of +0.38 e on the metal atoms. The preference of TMEDA·$LiBH_4$ for structure (**3**) can thus be readily understood as this arrangement offers a greater number of electron-rich hydrogen atoms for bonding to lithium than any monomeric structure. In addition, the calculations on the model species show that the η^3 bonding mode with its centrosymmetric arrangement of the BH_4 groups allows closer packing of the two BH_4 moieties and thus smaller Li---H and Li---B distances than those in the corresponding η^2 structure [for the η^3 structure Li---B = 2.584, Li---H (μ_3) = 2.147, and Li---H (μ_2) = 2.106 Å; for the η^2 structure Li---B = 2.861 and Li---H (μ) = 2.536 Å]. A qualitative estimate of the stabilisation of $(LiBH_4)_2$ by the TMEDA molecules is provided by calculations which show that the addition of four water molecules to $(LiBH_4)_2$ decreases the energy by 90.7 kcal mol^{-1} (1 cal = 4.184 J).

In conclusion, the lithium environments in compounds (**1**)—(**3**), in $LiBMe_4$,[14] and in many other molecular lithium alkyls,[15] amides, and imides[3] show how readily lithium can interact with more hydrogen atoms than simplistic LiHB or LiHC bond schemes might suggest. [For example, the metal co-ordination number in compounds (**1**),[4] (**2**),[5] and (**3**) is six, and is even higher than that in $LiBMe_4$.[14]] Moreover, the structures of compounds (**1**)—(**4**) reveal the dangers of treating BH_4^- ligands as sources of 2, 4, or 6 electrons depending on whether they are η^1, η^2, or η^3-co-ordinated.

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