

Lithium tetrahydroborate diethyl ether solvate $[\text{Et}_2\text{O} \cdot \text{LiBH}_4]_\infty$, a structure which consists of polymeric ribbons and contains μ_4 -hydrogen atoms¹

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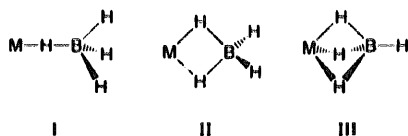
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Abstract

In the crystals of lithium tetrahydroborate, LiBH_4 , grown from ether solution at low temperatures, the polymeric $[\text{Li}_2(\text{BH}_4)_2]_n$ ribbon structure contains a μ_4 coordinated hydrogen atom; the crystal packing provides efficient shielding of the ribbon. © 1997 Elsevier Science S.A.

Alkali metal tetrahydroborates MBH_4 (M = alkali metal) are outstanding nucleophilic reducing reagents [1,2]. They are readily soluble in coordinating solvents such as liquid ammonia, amines and ethers. Compared to the essential synthetic applications [3–5], theoretical interest [6] and industrial utilisation relatively little attention has been given to their solvated structures. Up to now only the structures of $[\text{TMEDA} \cdot \text{LiBH}_4]_2$ [7,8] (TMEDA = tetramethylethylenediamine), $[\text{PMDETA} \cdot \text{LiBH}_4]$ [8] (PMDETA = pentamethyldiethylenetriamine), $[(18\text{-crown-6})(\text{LiBH}_4)_2]$ [9] and $[\text{diglyme} \cdot \text{NaBH}_4]_x$ [10] (diglyme = diethyleneglycoldimethylether) are known. In reactions in homogenous phase MBH_4 is frequently used in ether solutions. This encouraged us to study the ether/ LiBH_4 system in its own right, because it is known that this donating solvents have considerable influence on the reactivity of MBH_4 and hence affects its reaction pathway.



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¹ Dedicated to Professor Ken Wade on the occasion of his 65th birthday in recognition of his outstanding contributions to main group chemistry.

A major structural point of interest is the bonding mode between the BH_4 -residue and the alkaline metal cation. In transition metal tetrahydroborates terminal $\mu_2 \eta^1$ bonding (I) has been observed in $[(\text{MePh}_2\text{P})_3\text{CuBH}_4]$ [11], $\mu_2 \eta^2$ (II) in $[(\text{Ph}_3\text{P})_2\text{CuBH}_4]$ [12], $\mu_2 \eta^2 / \mu_3 \eta^2$ in $[\text{Co}(\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2)(\text{BH}_4)]$ [13,14] and $\mu_2 \eta^1$ (III) in $[\text{Zr}(\text{BH}_4)_4]$ [15]. Although theoretical studies on LiBH_4 predict the η^1 bonding mode of the BH_4^- moiety to be the energetically most favorable coordination to the metal [16,8], it has not yet been observed in coordination to alkaline metals. In the dimer of $[\text{TMEDA} \cdot \text{LiBH}_4]_2$ [7,8] the BH_4^- anion is η^2 coordinated by two lithium atoms. Four hydrogen atoms are μ_2 bridging lithium and boron and two are μ_3 bridging two lithium atoms and the boron atom. In $[(18\text{-crown-6})(\text{LiBH}_4)_2]$ [9] each BH_4^- anion is η^2 coordinated to a single lithium atom and both hydrogen atoms μ_2 bridge lithium and boron. In $[\text{diglyme} \cdot \text{NaBH}_4]_x$ [10] each BH_4^- anion is η^2 coordinated to two sodium atoms. One hydrogen μ_3 bridges both metals and boron while two bridge sodium and boron, each. The overall structure determining factor of the alkaline metal tetrahydroborate coordination seems to be the tendency to maximize the number of metal contacts to the electron-rich hydrogen atoms. Thus it seems surprising that μ_4 hydrogen coordination has never been observed neither in alkaline nor in transition metal tetrahydroborates.

This unprecedented bonding mode is observed in the structure of $[\text{Et}_2\text{O} \cdot \text{LiBH}_4]_\infty$. Crystals were grown from

a solution of lithium tetrahydroborate in ether at -45°C , and selected as well as transferred to the diffractometer at -60°C . Data were collected at -120°C . Once the crystals leave the mother liquor at temperatures slightly higher than -30°C they turn opaque due to loss of coordinated ether.

For the first time a single hydrogen atom of a BH_4^- residue bridges three metal atoms and the boron atom in a 4-center-2-electron bond. Fig. 1 illustrates the tetrahydroborate tetrahedron which is η^2 coordinated to three lithium atoms. While H_1 , H_2 and H_4 are μ_2 bridging one lithium atom and the boron atom, H_3 is μ_4 coordinated to all three lithium atoms and to boron. The μ_4 hydrogen atom H_3 provides the link to a polymeric structure which arises from adjacent fused four membered Li_2H_2 rings. The intriguing polymeric ribbon structure, akin a β -sheet structure known from proteins, is shown in Fig. 2. Along both backbones a lithium atom alternates with a BH_4 unit. The diethylether molecules frame the ribbon in an isotactical zigzag manner to opposite sides. The rhomboid Li_2H_2 rings display more acute endocyclic angles at the lithium atoms (av. $\text{Li}(\mu_4\text{H}_3)_2$ 82.2°) than at the hydrogen atoms (av. $\mu_4\text{H}_3\text{Li}_2$ 97.8°). The best plans of two adjacent rings are almost coplanar and intersect at an angle of 177.5° . The $\text{Li}-\text{H}_3$ distances along the backbone are 226(3) and 233(3) pm, respectively. The $\text{Li}-\text{H}_3$ link between the backbones is remarkably shorter (214(3) pm) but still longer than the $\text{Li}-\text{H}$ distances referring to μ_2 bridging (Li_1-H_2 197(3), $\text{Li}_{1a}-\text{H}_1$ 201(3) and $\text{Li}_{1b}-\text{H}_4$ 203(3) pm). As expected, the competition of three electropositive lithium atom for one single electron-rich μ_4 hydrogen atom results in longer $\text{Li}-\text{H}$ distances compared to the μ_2 bonding situation. The same is valid for the μ_3 (av. 209(3) pm)/ μ_2 (av. 204(3) pm) bonded hydrogen atoms in $[\text{TMEDA} \cdot \text{LiBH}_4]_2$ [7]. However, this point should not

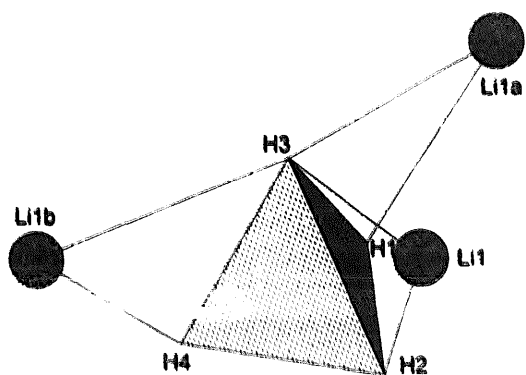


Fig. 1. The η^2 coordination of the three symmetry related lithium atoms to the BH_4^- tetrahedron in the structure of $[\text{Et}_2\text{O} \cdot \text{LiBH}_4]_x$. While H_1 , H_2 and H_4 μ_2 bridge one single lithium and the boron atom, H_3 μ_4 bridges all three lithium atoms and the boron atom ($\text{Li}_{1a} \cong -x+1, -y+1, z-1/2$; $\text{Li}_{1b} \cong -x+1, -y+1, z+1/2$).

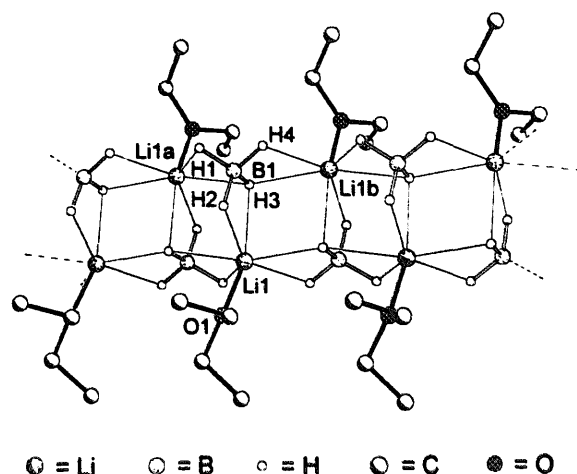


Fig. 2. The polymeric structure of $[\text{Et}_2\text{O} \cdot \text{LiBH}_4]_x$. Selected distances (pm) and angles ($^{\circ}$): Li_1-H_2 197(3), $\text{Li}_{1a}-\text{H}_1$ 201(3), $\text{Li}_{1b}-\text{H}_4$ 203(3), Li_1-H_3 214(3), $\text{Li}_{1a}-\text{H}_3$ 226(3), $\text{Li}_{1b}-\text{H}_3$ 233(3), Li_1-O_1 194.6(4), $\text{Li}_1 \dots \text{B}_1$ 249.2(5), $\text{Li}_{1a} \dots \text{B}_1$ 254.3(8); av. $\text{Li}(\mu_4\text{H}_3)_2$ 82.2° , av. $\mu_4\text{H}_3\text{Li}_2$ 97.8° .

be emphasized too much because of the uncertainty of hydrogen atom positions from X-ray data, high estimated standard deviations and the lack of neutron data. Nevertheless, the hydrogen atoms in the BH_4^- anion in general seem to be more attractive for $\text{Li}-\text{H}$ interactions [17–21] than those in BMe_3^- . Within the linear $\text{B}-\text{CH}_3-\text{Li}$ $\mu_2\eta^1$ coordination the $\text{Li}-\text{H}$ distances were determined from neutron data to be 223(1) and 221(2) pm from X-ray data [22].

Although the coordination number of each lithium atom in $[\text{Et}_2\text{O} \cdot \text{LiBH}_4]_x$ is seven, the coordination polyhedron can be described as a distorted tetrahedron. Three positions are occupied by $\eta^2\text{BH}_4^-$ anions while the fourth is attended by the oxygen atom of the ether molecule. The $\text{Li} \dots \text{B}$ distances along the backbone are 5 pm longer than across the backbones (254.3(8) and 249.2(5) pm, respectively).

Different to the bidentate donor base TMEDA the ether molecule provides one donor center to the electropositive lithium cation. Hence, it is reasonable to assume that this imposes remarkable changes in the solid state structures. While the employment of TMEDA yields dimeric molecules one should expect at least higher aggregates in ether if the second donor site of TMEDA is occupied by a third BH_4^- anion instead of a second ether molecule. The structure of $[\text{Et}_2\text{O} \cdot \text{LiB}_4]_x$ proves the basicity of the BH_4^- anion in the solid state to be higher than that of ether molecule. However, the existence of lower aggregates with higher ratios of ether in solution can not be ruled out based on solid state evidence alone.

The crystal packing shown in Fig. 3 elucidates the efficient shielding of charge-containing $[\text{Li}_2(\text{BH}_4)_2]_x$ sheets by the ether molecules. Each ribbon is isotactical zigzag coordinated by ether molecules at opposite sides

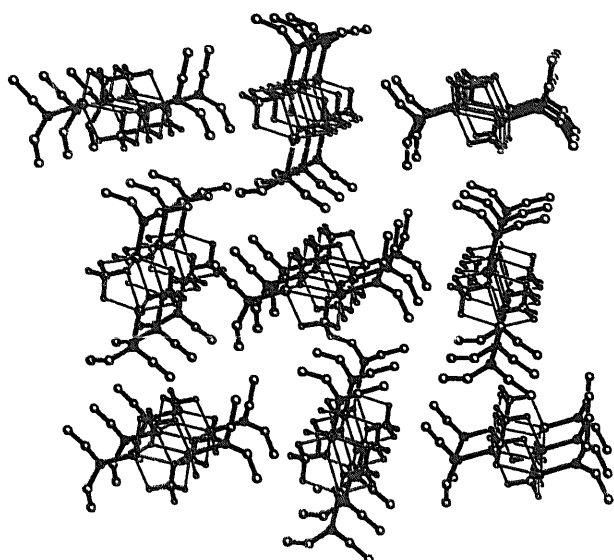


Fig. 3. Crystal packing of $[\text{Et}_2\text{O}\cdot\text{LiBH}_4]_n$ with the c -axis almost orthogonal to the paper plane.

(see also Fig. 2). This gives rise to polymeric plates with a hydrophobic 'coating' at the narrow sides. In the crystal this plates are turned by 90° and stacked on top of each other. The open side of the $[\text{Li}_2(\text{BH}_4)_2]_n$ sheets are shielded on top and below by coordinated ether coating of the plate. This explains the good solubility of LiBH_4 , once coordinated by ether, even in hydrocarbons.

1. Crystal structure determination

Crystal data for $[\text{Et}_2\text{O}\cdot\text{LiBH}_4]_n$, monomeric $\text{C}_4\text{H}_{14}\text{LiBO}$, colorless, crystal dimensions $0.95 \times 0.3 \times 0.15$ mm, $M = 95.90$, orthorhombic space group $\text{Pna}2_1$, $a = 1185.2(2)$, $b = 1359.2(2)$, $c = 454.1(1)$ pm, $V = 0.7315(2)$ nm³, $Z = 4$, $\rho_{\text{calc}} = 0.871$ g cm⁻³, $\mu = 0.053$ mm⁻¹, $F(000) = 216$, 1495 reflections collected ($9 \leq 2\theta \leq 60^\circ$) at 153(2) K, 1255 independent ($R_{\text{int}} = 0.071$), all used in the structure refinement; $R_1 = 0.070$ [$I > 2\sigma(I)$], $wR_2 = 0.158$ (all data), $\text{good} = 1.019$ for 80 parameters and no restraints, largest difference

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$) for 1. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
B ₁	4599(2)	3952(2)	2302(12)	28(1)
Li ₁	4483(4)	5783(3)	2303(17)	31(1)
O ₁	3055(1)	6486(1)	2087	32(1)
C ₁	1250(2)	5635(2)	1906(14)	48(1)
C ₂	2087(2)	6195(2)	3729(8)	34(1)
C ₃	2934(3)	7387(2)	480(10)	37(1)
C ₄	3222(3)	8264(2)	2316(14)	51(1)

Table 2

Selected bond lengths (pm) and angles ($^\circ$) for 1

B ₁ –Li ₁	249.2(5)	B ₁ –Li ₁ ^a	254.3(8)
B ₁ –Li ₁ ^b	254.3(8)	B ₁ –H ₁	113(4)
B ₁ –H ₂	118(3)	B ₁ –H ₃	117(3)
B ₁ –H ₄	117(4)	Li ₁ –O ₁	194.6(4)
Li ₁ –Li ₁ ^a	334.4(6)	Li ₁ –H ₂	197(3)
Li ₁ –H ₃	214(3)	O ₁ –C ₂	142.5(3)
O ₁ –C ₃	143.3(3)	C ₁ –C ₂	150.0(5)
C ₃ –C ₄	149.5(5)		
Li ₁ –B ₁ –Li ₁ ^a	83.2(2)	Li ₁ ^a –B ₁ –Li ₁ ^b	126.5(2)
Li ₁ –B ₁ –H ₁	126(2)	Li ₁ ^a –B ₁ –H ₁	50(2)
Li ₁ ^b –B ₁ –H ₁	143(2)	Li ₁ –B ₁ –H ₂	50.6(14)
Li ₁ ^a –B ₁ –H ₂	104(2)	Li ₁ ^b –B ₁ –H ₂	106(2)
H ₁ –B ₁ –H ₂	110(3)	Li ₁ –B ₁ –H ₃	59.2(14)
Li ₁ ^a –B ₁ –H ₃	63(3)	Li ₁ ^b –B ₁ –H ₃	66(3)
H ₁ –B ₁ –H ₃	107(3)	H ₂ –B ₁ –H ₃	110(2)
Li ₁ –B ₁ –H ₄	124(2)	Li ₁ ^a –B ₁ –H ₄	148(2)
Li ₁ ^b –B ₁ –H ₄	51(2)	H ₁ –B ₁ –H ₄	110(2)
H ₂ –B ₁ –H ₄	107(3)	H ₃ –B ₁ –H ₄	113(3)
O ₁ –Li ₁ –B ₁	122.6(2)	O ₁ –Li ₁ –B ₁ ^b	116.7(3)
B ₁ –Li ₁ –B ₁ ^b	96.8(2)	O ₁ –Li ₁ –B ₁ ^a	104.9(3)
B ₁ ^b –Li ₁ –B ₁ ^a	126.5(2)		

^{ab} Symmetry transformations used to generate equivalent atoms: (a) $-x+1, -y+1, z-1/2$; (b) $-x+1, -y+1, z+1/2$.

peak/hole = 201/–170 e nm⁻³. The data were collected on a Stoe–Siemens AED four-circle diffractometer (graphite-monochromated Mo–K α radiation, $\lambda = 0.71073$ Å), equipped with a modified version of the Siemens/Nicolet LTIIa low temperature device [23]. Due to thermal sensitivity of the crystals they were mounted at -60°C in an oil drop and shock-cooled at the tip of a fibre [24]. The structures were solved by direct methods (SHELXS-90) [25] and refined by full-matrix least squares methods against F^2 employing all data (SHELXL-96) [26]. Anisotropic refinement of all non-H atoms was performed. B bonded hydrogen positions were located by difference Fourier synthesis and refined isotopically; no constraints or restraints were applied. H atoms of the ether molecule were included on calculated positions and treated riding with the isotropic parameters constrained to equal 1.2 times $U(\text{equivalent})$ of the attached carbon atom. Definition of R -values: $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. Further crystallographic details, atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Center. See Tables 1 and 2.

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