Metal Hydroborates and Hydroborato Metalates, 21[◇]

Solvates of Lithium (Dimethylamino)trihydroborate[☆]

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Li(Me$_2$NBH$_3$) (1) was prepared by deprotonation of Me$_2$NH · BH$_3$ with LiBu and its solubility determined in various solvents. Compound 1 is unstable in most ethereal solvents and decomposes in a reversible reaction into LiH and Li(Me$_2$N−BH$_2$−NMe$_2$−BH$_3$) (2). Five solvates of 1 were characterised by X-ray structure analysis. Li(Me$_2$NH$_3$) · TMEDA is a dimer in the solid state, and two units are connected to one another by B−H···Li bonds. The crystal structure of Li(Me$_2$NBH$_3$) · 0.5 dioxane is represented by layers consisting of tetrameric Li(Me$_2$NBH$_3$) units connected via dioxane molecules. Each Li atom is coordinated to one oxygen atom, one nitrogen atom, and two hydrogen atoms. Also Li(Me$_2$NBH$_3$) · 0.5 O$_2$C$_3$H$_6$ forms an extended layer, however with pentacoordinated Li atoms which bear one oxygen, one nitrogen, and three hydrogen atoms. A similar layer structure was also found for Li(Me$_2$NBH$_3$) · O$_3$C$_3$H$_6$ where each Li atom is bound to two oxygen atoms of different trioxane molecules, one nitrogen atom, and two hydrogen atoms. Finally, Li(Me$_2$NBH$_3$) · 12-crown-4 retains its molecular integrity in the solid state. Its Li atom is pentacoordinated by four oxygen atoms and one nitrogen atom.

Although alkali metal (dialkylamino)trihydroborates are known since 1961[2,3] they have received little attention until recently[4,5]. This renewed interest is associated with their use as powerful but also selective reducing reagents in organic synthesis[4,5]. Nevertheless, our knowledge of their structure as well as our knowledge of their solution state is only marginal although they are well-defined by their ^{11}B-NMR data[5]. In contrast to the structures of metal tetrahydroborates which contain μ_1-BH$_4$, μ_2-BH$_4$, and μ_3-BH$_4$ groups[7], the structure of metal aminotrihydroborates may be even more variable because one can expect the formation of B−N−M (M = metal atom) units besides B(H)$_n$M interactions. Li(Me$_2$NBH$_3$) seemed to be a suitable model compound to study this aspect.

Synthesis and Physical Properties of Li(Me$_2$NBH$_3$)

Li(Me$_2$NBH$_3$) (1) was readily synthesised by the known deprotonation of Me$_2$NH · BH$_3$[6] with LiBu in hexane[5] as depicted by eq. (1). However, small amounts of Bu$_2$BNMe$_2$, B(NMe$_2$)$_3$, and LiBBu$_4$ are also formed as shown by ^{11}B-NMR spectroscopy. The formation of these species is formally described by eqs. (2) to (4). The solvates Li(Me$_2$NBH$_3$) · 0.5 dioxane, Li(Me$_2$NBH$_3$) · 0.5 dioxolane, Li(Me$_2$NBH$_3$) · trioxane, and Li(Me$_2$NBH$_3$) · 12-crown-4 were obtained by adding the ether ligand to a solution of Me$_2$NH · BH$_3$ in toluene followed by deprotonation of the amine−borane with butyllithium.

[◇] Part 20: Ref.[1].

$$Me_2NH \cdot BH_3 + LiBu \rightarrow Li(Me_2NBH_3) + BuH \qquad (1)$$
$$\mathbf{1}$$

$$1 + 2\,LiBu \rightarrow 3\,LiH + Bu_2BNMe_2 \qquad (2)$$

$$3\,Bu_2BNMe_2 \rightarrow 2\,BBu_3 + B(NMe_2)_3 \qquad (3)$$

$$BBu_3 + LiBu \rightarrow LiBBu_4 \qquad (4)$$
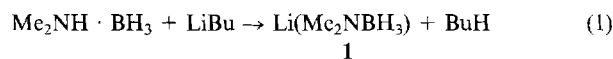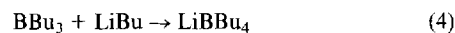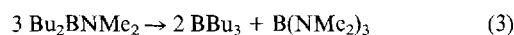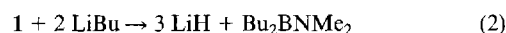
Figure 1. Schematic representation of the solubility of Li(Me$_2$NBH$_3$) (1) in various solvents and at different temperatures

Solubility of Li[Me$_2$NMH$_3$] in g/l
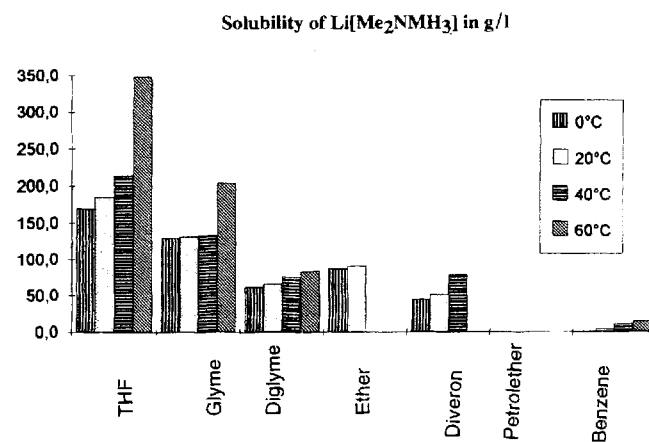
Compound 1 is insoluble at ambient temperature in pentane and hexane but slightly soluble in benzene and toluene. Figure 1 depicts the temperature-dependent solubility of 1 in several solvents. Obviously, THF is the best solvent, and 3 M solutions can be prepared at 20 °C, corresponding to a solubility of 194 g of 1 per litre. This high solubility is certainly due to the formation of solvates, and so far Li-

$(Me_2NBH_3) \cdot 0.5$ THF, $Li(Me_2NBH_3) \cdot 0.5$ dioxane, and $Li(Me_2NBH_3) \cdot$ glyme were isolated from the solutions.

Chemical Properties

Compound **1** reacts rapidly and quantitatively with water as shown in eq. (5) followed by slow further hydrolysis with hydrogen evolution. Therefore, reaction (5) can be used for the determination of **1** by acidimetric titration.

$$Li(Me_2NBH_3) + H_2O \rightarrow LiOH + Me_2NH \cdot BH_3 \qquad (5)$$
$$\mathbf{1}$$

$$Me_2NH \cdot BH_3 + 3\ H_2O \rightarrow Me_2NH + B(OH)_3 + 3\ H_2 \qquad (6)$$

$$2\ Li(Me_2NBH_3) \rightleftharpoons LiH + Li(Me_2N-BH_2-NMe_2-BH_3) \qquad (7)$$
$$\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{2}$$

The most noticeable property of **1** is its instability in ethereal solvents. As was first detected by Keller[8] there exists an equilibrium (7) in diethyl ether solution between **1** and LiH and the more complex diaminodiborate **2**. The ^{11}B-NMR signal of the BH_3 group of **2** is difficult to detect because it is almost isochronous with that of **1**. However, this group can be unambiguously detected at 40 °C with a high-field instrument. The triplet in the proton-coupled spectrum for the BH_2 group in **2**, on the other hand, is readily observed at $\delta^{11}B \approx 4$. The equilibrium (7) not only depends on the solvent but also on its establishment with time.

In benzene and ether the equilibrium (7) is almost "instantaneously" achieved, and the equilibrium constant $K \approx [Li(Me_2NBH_2NMe_2BH_3]/[Li(Me_2NBH_3)]$ in ether was determined as $K = 1$. No change in concentration was observed in glyme solutions after three days, and K is approximately 25. The equilibrium is reached after 10 days by using diglyme as solvent while **1** is most stable in THF solution: only 2% decompose within two months. An even higher stability of **1** is achieved by dissolving the adduct $\mathbf{1} \cdot$ TMEDA in benzene: no decomposition was observed.

Figure 2 demonstrates the solubility of $Li(Me_2NBH_3) \cdot$ TMEDA in various solvents. Most noticeable is the solubility of this adduct in petroleum ether. Moreover, its solubility in diethyl ether is considerably increased as compared to **1** while its saturation concentration in THF is $\approx 50\%$ less than for **1**. Nevertheless, the solutions of $\mathbf{1} \cdot$ TMEDA are also unstable, and decomposition occurs as for **1**. Least stable solutions were obtained with hexane and diethyl ether as solvents, and a much higher stability was observed in THF but in diglyme no decomposition according to eq. (7) could be detected by ^{11}B-NMR spectroscopy.

NMR Spectra

The solution state of **1** and $\mathbf{1} \cdot$ TMEDA can be evaluated by NMR spectroscopy. Table 1 compiles the observed chemical shifts and coupling constants.

There exists a small but significant difference both for the shielding of the ^{11}B nucleus and the coupling constant, depending on the solvent. In less polar solvents the boron nucleus of **1** is less shielded and the coupling constant somewhat larger than in more polar and better coordinat-

Figure 2. Solubility of $(H_3BNMe_2)Li \cdot$ TMEDA in various solvents and at different temperatures

Solubility of TMEDA - Adducts in g/l

Table 1. NMR data of the isolated $Li(Me_2NBH_3)$ solvates in solution and of $Li(Me_2N-BH_2 \cdot NMe_2-BH_3)$. * Only the signal at the BH_2 group is indicated. That for the BH_3 group overlaps the ^{11}B-NMR signal of $Li(Me_2NBH_3)$

	Ether	THF	Glyme	Diglyme	Benzene	Hexane
Li(Me₂NBH₃)						
$\delta^{11}B$	−14	−15	−13.8	−14.6	−13.5	—
$^1J(^1H^{11}B)$	86	87	88	87	86	—
δ^7Li	—	0.548	—	0.498	—	—
Li(Me₂NBH₂NMe₂BH₃)						
$\delta^{11}B$*	3.7	1.8	4.4	—	3.2	—
$^1J(^1H^{11}B)$	103	96	97	—	103	—
Li(Me₂NBH₃) · 0.6 THF						
$\delta^{11}B$	−14.0	—	—	—	—	—
$^1J(^1H^{11}B)$	78	—	—	—	—	—
δ^7Li	−3.62	—	—	—	—	—
Li(Me₂NBH₃) · TMEDA						
$\delta^{11}B$	−14.7	−15.0	−14.5	—	−14.6	−14.4
$^1J(^1H^{11}B)$	86	87	87	—	87	88
δ^7Li	—	—	—	—	—	−0.047

ing solvents. Moreover, also the shielding of the ^7Li nucleus depends, not unexpectedly, on the nature of the solvent.

A single signal is observed for the Me_2N group of **1** in benzene in the ^1H-NMR spectrum as well as a 1:1:1:1 quartet for the BH_3 protons. Compared with $Me_2NH \cdot BH_3$ ($\delta^1H = 1.93$) the CH_3 resonance of **1** is observed at lower field ($\delta = 2.61$). If an uncoordinated Me_2N group was present in **1**, then a high-field shift would be observed due to the increased negative charge at the nitrogen centre. Therefore, the deshielding suggests the presence of a Me_2N group of ammonium-type character, and this can be rationalised not only by the presence of a B−N but also by the occurrence of an N−Li bond.

Although a smaller variation of $\delta^{11}B$ was observed for **1** $\cdot$ TMEDA in various solvents as compared to **1**, $^1J(^{11}B^1H)$ remains constant, and these data indicate that $\mathbf{1} \cdot$ TMEDA does not change its nature in any of the solutions investigated. Moreover, the excellent shielding of the ^7Li nucleus of **1** $\cdot$ TMEDA, as observed for its hexane solutions, indicates the presence of ion pairs and strong interactions of the Li centre with the TMEDA ligand.

$\delta^{11}B$ of the BH_3 group in **2** is found at lower field (δ = 0.2–0.3) than that of this group in **1** in the same solvent. However, the shielding of the boron nucleus of the BH_2 group varies both in its δ value and the coupling constant $^1J(^{11}B^1H)$. The latter indicates more s character of the bonds in **2** as compared to its BH_3 group in **1**.

Besides the characterization of **1** and **1** · TMEDA by NMR data, the only structurally relevant feature that can be extracted from the NMR data is that the nitrogen atoms of the Me_2N groups are tetracoordinated. No information can be derived whether the BH_3 group participates in bonding to the Li centre, because the quartets observed indicate that all three hydrogen atoms of the $Me_2NBH_3^-$ anion are chemically equivalent. For this reason crystal structures had to be determined. A similar behaviour is known for the BH_4 groups in metal tetrahydridoborates[7], which show quintets in their ^{11}B-NMR spectra even for typical covalent molecules such as $Al(BH_4)_3$. Therefore, the structure of the solvates in the solid state were determined by X-ray structure analysis.

Crystal and Molecular Structures

$Li(Me_2NBH_3)$ · TMEDA shows the presence of a centrosymmetric dimer in the crystal structure. Figure 3 depicts the structure of this molecule. Relevant structural parameters are summarised in Table 2.

Figure 3. Molecular structure of the centrosymmetric dimeric unit of $Li(Me_2NBH_3)$ · TMEDA
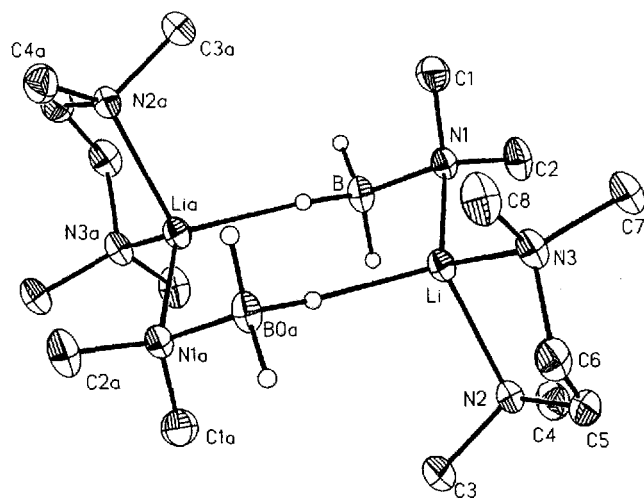
Table 2. Selected bond lengths [Å] in $Li(Me_2NBH_3)$ solvates. Estimated standard deviations are given in parenthesis

	TMEDA	1,4-Dioxane	1,3-Dioxolane	1,3,5-Trioxane	12-Crown-4	
Li–N	2.004(4)	2.024(4) 2.020(5)	2.041(5) 2.030(5)	2.035(7)	1.999(8) Li1	2.004(8) Li2
N–B	1.552(3)	1.534(4) 1.533(4)	1.541(4) 1.543(4)	1.52(6)	1.555(6) Li1	1.562(6) Li2
Li···B	2.268(4)	2.590(4) 2.742(5)	2.489(5) 2.494(5)	2.806(8) 2.404(8)	2.82(1) Li1	2.58(1) Li2
Li–O(N)	2.118(4) 2.138(4)	2.068(4) 2.093(4)	2.063(5) 2.066(5)	2.034(7) 2.082(7)	2.138(8) Li1 2.159(8) 2.058(7) 2.192(8)	2.157(8) Li2 2.152(8) 2.138(8) 2.194(8)
Li···H	2.003	1.978 (Li2)H2A 1.906 (Li1)H2B	1.879 2.008	1.917 2.127	2.82 (H2F)	2.59 (H1B)

The Li–N bond lengths to the TMEDA unit are, on average, 0.12 Å longer than to the Me_2N group, and a fairly small bite angle of only 87.3(2)° results for the TMEDA group. The N1–Li–N3 and N1–Li–N2 bond angles [117.3(2) and 123.9(2)°] are much wider, and, consequently, the H···Li–N bond angles are also very different [99.7–118.0(8)°]. Thus, the tetracoordination at the Li centre deviates significantly from an ideal tetrahedral environment. The B–N bond length of 1.552(3) Å is typical of BN single bonds between tetracoordinated atoms substantiated by a comparison with the BN bond length in cubic boron nitride (1.554 Å)[9]. However, the B–N–Li bond angle is only 94.9(2)°, in contrast to the bond angles at the boron atoms which do not deviate strongly from the ideal tetrahedral angle [107.7(13)–111.0(13)°]. Nevertheless, the hydrogen atom involved in the Li···H–B interaction can be readily recognised by a somewhat longer B–H bond, although all three B–H bond lengths 1.15(3), 1.13(3), and 1.17(3) Å must be considered to be not much different.

Figure 4. Association of two units $[Li(Me_2NBH_3)]_2$ · $O_2C_4H_8$ with formation of a $Li(Me_2NBH_3)$ tetramer
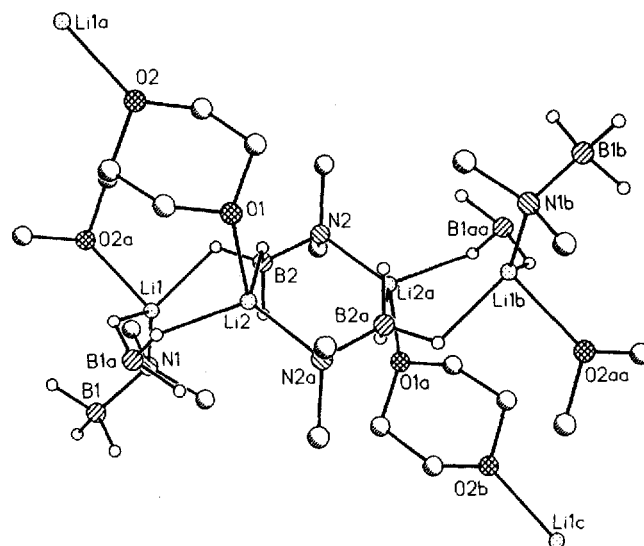
In contrast to **1** · TMEDA the dioxane solvate **1** · 0.5 $O_2C_4H_8$ possesses a more complex structure. Figure 4 describes the association of two molecules. It reveals that each oxygen atom of the dioxane molecule associates with one Li centre of a $Li(Me_2NBH_3)$ molecule, which also interacts with the nitrogen atom of the Me_2NBH_3 anion. Therefore, the composition of a hemisolvate is easily rationalised. Figure 4 also shows tetracoordinated boron and nitrogen atoms and the coordination at the Li atoms.

If the Li centres become tetracoordinated as in **1** · TMEDA, it is conceivable that two hydrogen bonds are required to achieve this. This is exactly what happens. As a consequence, tetrameric $[Li(Me_2NBH_3)]_4$ units are formed where two hydrogen atoms of a BH_3 group are involved in the formation of Li···H–B bonds. The tetrameric units (see Figure 5) are joined to form an extended chain, and these chains are connected by dioxane molecules to form a layer.
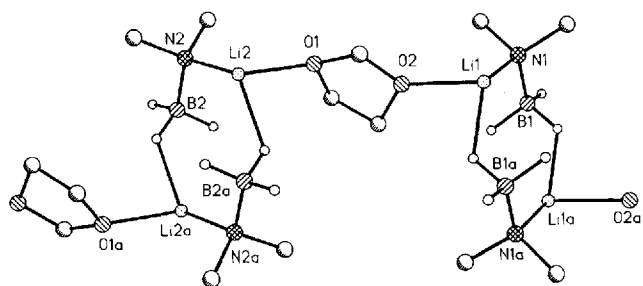
These layer are stacked on top of one another in the [001] plane.

Figure 5. Representation of a part of the layered structure of [Li(Me₂NBH₃)]₂ · O₂C₄H₈

Figure 7. The layer structure of [Li(Me₂NBH₃)]₂ · O₂C₃H₆
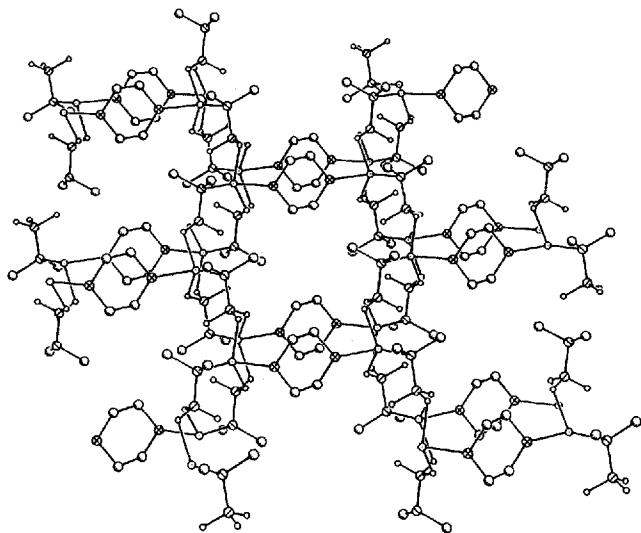
Similar to the dioxane solvate of Li(Me₂NBH₃) a hemisolvate Li(Me₂NBH₃) · 0.5 O₂C₃H₆ is formed with 1,3-dioxolane. Since the oxygen atoms of the solvent molecule are not "*trans*" to one another as in dioxane, a structure differing from the dioxane solvate was to be expected. Figure 6 represents the association of the molecular units. As shown, each oxygen atom of the dioxolane coordinates to a Li atom of a Li(Me₂NBH₃) unit which is also coordinated to the N atom of a dimethylamino group. Both Li−O atom distances have to be considered to be of equal length [2.063(5) and 2.066(5) Å]. However, the Li−N distances seem to be slightly different [2.041(5) to Li1, and 2.030(5) Å to Li2]. On the other hand, the B−N bond in the two non-equivalent Me₂NBH₃⁻ units are equally long [both 1.54(4) Å]. There are Li···H contacts between the "dimeric" [Li(Me₂NBH₃)]₂ entities with singly bridging Li···H contacts (see Figure 6), having Li···H and H−B atom distances of 1.92(3) and 1.18(3) Å. In addition, there is a somewhat longer Li···H contact of 2.13(3) Å.

ordinated by two oxygen and two hydrogen atoms as well as one nitrogen atom (see Figure 7).

In contrast to the hemisolvates of Li(Me₂NBH₃) with dioxane and dioxolane, 1,3,5-trioxane forms a 1:1 adduct with **1** thus providing formally three oxygen atoms for coordination with each Li atom. Consequently, we meet a structure as depicted in Figure 8. A chain is formed from [Li(Me₂NBH₃] · O₃C₃H₆ molecules, and this chain coordinates to a second chain by making use of a second oxygen donor atom of the trioxane molecule. Repetition of this process leeds finally to an extended layer as demonstrated in Figure 9.

Figure 8. Association of Li(Me₂NBH₃) · O₃C₃H₆ units by Li···H−B bonds. An infinite chain is formed this way

Figure 6. Association of two units of [Li(Me₂NBH₃)]₂ · O₂C₃H₆

The "dimeric units" are expanded to extented layers of [Li(Me₂NBH₃)]₂ · O₂C₃H₆ units which are arranged parallel to the [001] plane. In this structure each Li atom is pentaco-
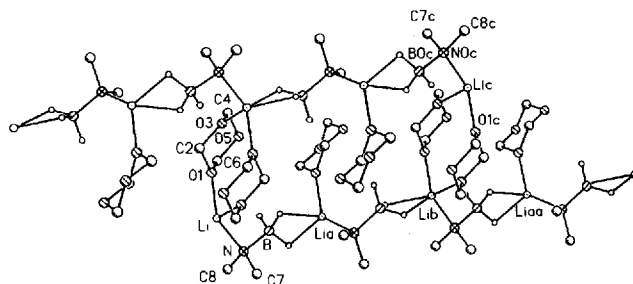
Figure 9. Expansion of the chains shown in Figure 8 to a layer structure by Li−O coordination
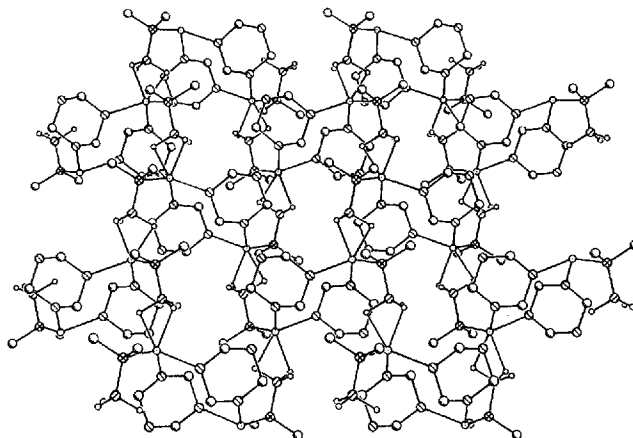
Only two of the three oxygen atoms of the trioxane coordinate to Li atoms whereby the ether molecule connects strings of the lithium (dimethylamino)trihydroborate molecules. Each Li atom in the extended structure is pentacoordinated by two oxygen and two hydrogen atoms as well as one nitrogen atom in analogy to the hemidioxolane.

In addition, two Li⋯H distances should be noted. The large one [2.806(8) Å] which represents of course no bonding interaction, is directed to the boron atom of the "monomeric units", while the second one is much shorter [2.404(8) Å], and this hydrogen atom belongs to the boron atom that forms the "double hydrogen" bonds with the Li centre.

The crown complex Li(Me$_2$NBH$_3$) · 12-crown-4 crystallises in the monoclinic system, space group $P2_1/n$, and the asymmetric unit contains two independent molecules. One is shown in Figure 10 in a view approximately downward the Li−N axis. Each Li atom is connected to four oxygen atoms of the crown ether to generate a slightly distorted tetragonal pyramid. The Li−O atom distances range from 2.058(7) to 2.192(8) Å for Li1 and from 2.138(8) to 2.194(8) Å for Li2 with O−Li−O bond angles ranging from 78.3(3) to 80.4(3)° for Li1 and from 77.8 to 79.1(3)° for atom Li2. Therefore, the LiO$_4$ cores of the two molecules are rather similar. In addition, each Li atom is coordinated to the nitrogen atom of its Me$_2$NBH$_3$ unit with identical Li−N bonds lengths [1.999(8) and 2.004(8) Å]. However, the two molecules differ significantly with regard to the Li⋯B distance which is 2.82(1) Å for Li1 and 2.58(1) Å for Li2. This difference is due to the larger tilt of the Li−N bond versus the O$_4$ plane which is 7.2° for Li1−N1 and 18.6° for Li2−N2.

Figure 10. Molecular structures of one of the two independent Li-(Me$_2$NBH$_3$) · 12-crown-4 molecules. View downwards along the LiN axis
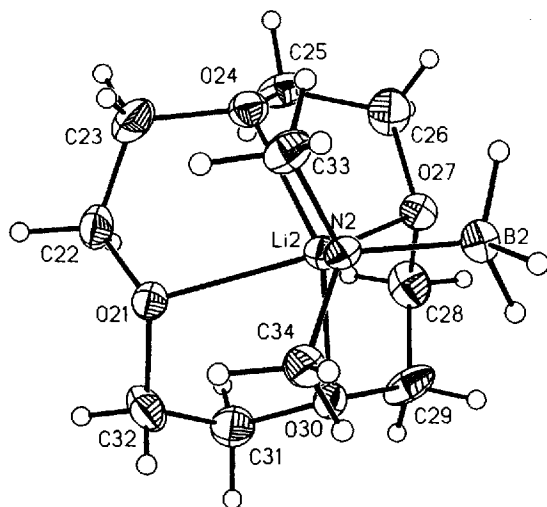
The most important structural feature of the molecular structure of the crown ether complexes is the absence of any Li⋯H interactions which is so characteristic of all the other solvates of Li(Me$_2$NBH$_3$) studied so far. The closest Li⋯H distances are 2.82(4) Å for Li1⋯H(1)F and 2.59(4) Å for Li2⋯H(2)B.

IR Spectra

It should be possible to analyse the IR spectra of the Li(Me$_2$NBH$_3$) solvates in the BH stretching region by using the information given by the structures obtained by X-ray methods. Figure 11 shows the region of the BH-stretching bands. The free Me$_2$NBH$_3$ anion may have local C_{3v} symmetry for its BH$_3$ component or C_s point group symmetry for the anion. For the first case two stretching vibrations v_s and v_{as}BH$_3$ are to be expected, for the second case three bands can be assigned to v_{as}BH$_2$ and v_sBH$_2$ as well as to vBH. The latter symmetry would also hold if a single Li⋯H−B bond was present. In addition, the stretching bands should have shoulders on the high-frequency side due to the ^{10}B isotope for boron. Coupling of the BH stretching vibrations with the BN stretching mode is unlikely. Since 1 · 12-crown-4 contains unbridged anions its IR spectrum could be the prototype. However, the IR spectra which were recorded for solid samples show that a total of 10 bands are present. If we take the most prominent bands at 2298 and 2218 cm^{-1} with satellites at 2333 and 2259 cm^{-1} into account than these bands are the most likely candidates for v_{as}BH$_3$ and v_sBH$_3$. The band at 2359 cm^{-1} might result from a combination of strong bands located at 1095 and 1257 cm^{-1} while the band at 2182 cm^{-1} could result as overtone of the strong band at 1097 cm^{-1}. Such combinations are well-known from the IR spectra of alkali metal tetrahydroborates[7].

The most simple structure next to the crown ether solvate is dimeric [Li(Me$_2$NBH$_3$) · TMEDA] with its single hydrogen bonds. Its IR spectrum in the BH stretching region shows only four prominent bands. However, the band at 2208 cm^{-1} is quite broad, but could not be better resolved. It may be due to v_{as}BH$_2$ while v_sBH$_2$ could be represented by the band at 2303 cm^{-1} with the ^{10}B satellite at 2329 cm^{-1}. Consequently, the band at 2059 cm^{-1} can be assigned to be "bridging" BH bond.

The X-ray structure of the dioxane solvate reveals two Li⋯H−B interactions for each Me$_2$NBH$_3$ group. The strongest IR band of this solvate is at highest frequency, and no shoulders due to corresponding ^{10}BH$_n$ vibrations can be observed. This also holds for the other three bands which have all to be considered to be of strong to medium-strong intensity.

In contrast, the region of the BH stretching vibrations covers a larger range for the dioxolane and trioxane solvates. Characteristic is a high-frequency band at ≈2360 cm^{-1} which could be due to the BH bond whose hydrogen is not in contact with a Li atom. Since there are two non-equivalent Li(Me$_2$NBH$_3$) units present is the solid-state structures one may tentatively assign the two very strong bands at 2260 and 2221 cm^{-1} to v_{as}BH$_2$ vibrations. Finally, the IR spectrum of solvent-free Li(Me$_2$NBH$_3$) shows three strong bands and two of medium intensity. This can be taken as evidence for stronger Li⋯H−B interactions as compared to those in the solvates. All in all, no significantly strong Li⋯H−B interaction as found for typical covalent hydroborates[7] are revealed by the IR spectra of 1 and its solvates.

Figure 11. IR spectra of Li(Me$_2$NBH$_3$) solvates recorded as Hosta-flon/Nujol mulls. a) 12-crown-4-solvate, b) TMEDA solvate, c) tri-oxolane solvate, d) dioxolan solvate
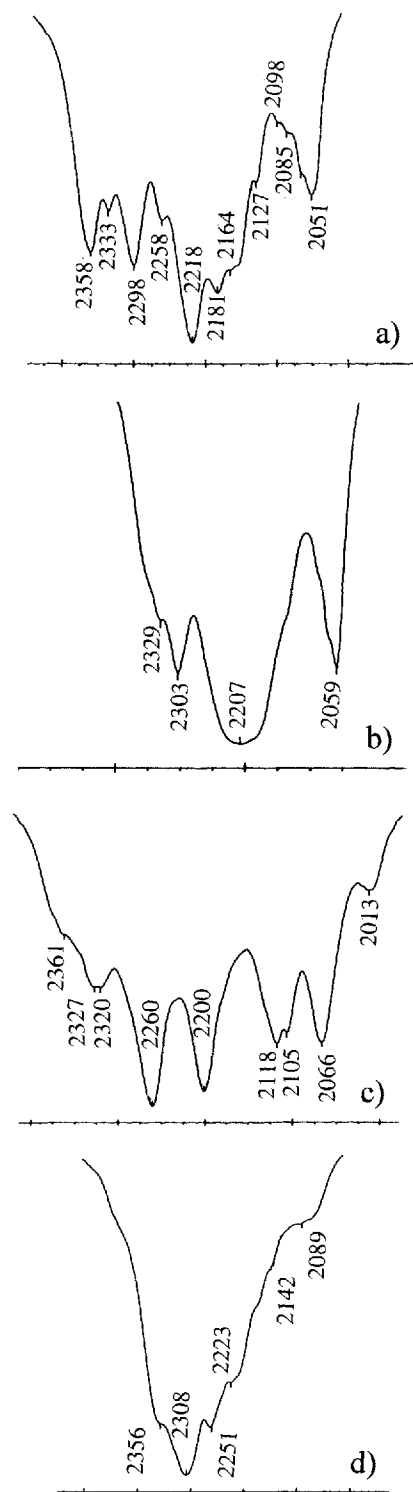
poses into LiH and Li(Me$_2$NBH$_2$−NMe$_2$−BH$_3$) (2). The amino group in this more complex anion is probably less basic than in the parent compound due to the negative charge spread over a larger anion. A decomposition of this larger anion into LiH and Li[Me$_2$N(BH$_2$−NMe$_2$)$_n$BH$_3$] or LiH and [Me$_2$NBH$_2$]$_n$ was not observed either in our study or in previous investigations[8,10]. The decomposition seems to be initiated by attack of the Li ion on a hydridic hydrogen atom, and this attack is the more retarded the stronger the Li centre interacts with a polar solvent molecule. This is demonstrated by the fairly stable solution of 1 in THF or by the stability of the 12-crown-4 complex. However, the structures of four out of five solvates of 1, determined by X-ray methods, clearly indicate that these are determined by Li⋯H−B interactions.

The structural characteristics of all solvates is the presence of Li−N interactions. The bond lengths range from 1.999(8) in 1 · 12-crown-4 to 2.041(5) Å in 1 · dioxolane, and these fall into the region found for lithium amides LiNR$_2$ and LiN=CR$_2$[11], but are shorter than for solvates of monomeric LiNR$_2$ compounds. They resemble more closely those of solvated dimeric lithium amides [LiNR$_2$L]$_2$ (L = OEt$_2$, TMEDA)[11]. In these compounds the Li centre is usually tetracoordinated while the Li atoms in the 1 solvates also adopt pentacoordination. Normally, the increase in coordination is accompanied by increasing atom-to-atom distances in the coordination polyhedron. From this point of view the class of compounds described here must have fairly strong Li−N bonds. The Li−O atom distances are somewhat longer than the Li−N bonds and are longest in the crown ether solvate. The Li−O distances are also longer than found for monomeric Li(SCN) · 12-crown-4 (2.08 Å)[12]. The Li−O bond length for 1 · 0.5 O$_2$C$_4$H$_8$ corresponds with those found for Li$_3$CrMe$_6$ · 1.5 dioxane[13] (2.06 Å). Table 2 lists also the closest Li⋯H−B and Li⋯B distances. One should be aware that the precision with which the hydrogen atom positions (and those of the Li atoms as well) can be determined by X-ray crystallography is much less than for the atoms of the elements of the second period of the periodic system. These Li⋯H distances are usually smaller than the Li⋯H atom distance determined for LiH (2.04 Å). Finally, the Li⋯B distances vary considerably, but many of them are close to the sum of their atomic radii (2.39 Å). The data can be compared with those of (mes$_2$BH$_2$)Li · 2 DME (DME = 1,2-dimethoxyethane; Li⋯H 2.06 Å), a lithium hydroborate that contains hexacoordinated Li atoms[14]. Thus, all evidence points to a high degree of polarity between the solvated Li cations and the Me$_2$NBH$_3$ anions. The packing of atoms around the Li centres is rather asymmetric for the pentacoordinated atoms which leads to fairly open structures in the solid state.

Discussion

Lithium (dimethylamino)trihydridoborate (1) is an interesting substituted hydroborate whose Me$_2$N group is a strong base, because it initiates Li−N bonding. It decom-

Experimental

All experiments were carried out under anhydrous conditions by using Schlenk techniques. – Solvents were dried according to conventional methods and stored under dry nitrogen. – NMR: Bruker WP 200 (^{11}B), Jeol GSX 270 (^{1}H, ^{13}C), Jeol EX 400 (^{7}Li). – IR: Nicolet FT-IR (Nujol-Hostaflon suspension for the solids). – Elemental analyses: Microanalytical laboratory of our institute.

Preparation of Li(Me$_2$NBH$_3$) (1): 150 ml of a 1.56 M solution of LiBu in hexane was added to a vigorously stirred suspension of Me$_2$NH · BH$_3$ (12.4 g, 210 mmol) in 100 ml of hexane within 2.5 h. An exothermic reaction occurred with formation of a voluminous solid. After stirring for 4 h, the solid was separated from the liquid phase by centrifugation and washed twice with 50 ml of hexane each. After drying in vacuo the yield was 13.1 g (96%). The solution showed the following signals in the ^{11}B-NMR spectrum: δ = 45.8 (Bu$_2$BNMe$_2$), 27.8 [B(NMe$_2$)$_3$], and LiBBu$_4$ (–18.1) in an approximate ratio of 1:4:2. – C$_2$H$_9$BLiN (64.85): calcd. C 37.05, H 13.99, N 21.6; found C 37.77, H 13.96, N 21.17.

Preparation of Li(Me$_2$NBH$_3$) · 0.5 THF: Me$_2$NH · BH$_3$ (12.37 g, 210 mmol) was dissolved in 100 ml of tetrahydrofuran and the solution cooled with an ice bath. 150 ml of a 1.56 M hexane solution of LiBu (230 mmol) was added with vigorous stirring within 2 h. After the addition had been completed, the reaction mixture was allowed to attain ambient temp. After stirring for an additional 2 h a 50-ml portion of hexane was added to complete the precipitation of Li(CH$_3$)$_2$NBH$_3$ · n THF. The solid was separated by centrifugation and washed twice with 100 ml of hexane each. After

drying in vacuo (0.1 mm Hg) for 3 h the yield was 8.2 g (60%). The white powdery material decomposed in a sealed capillary at ≈ 90°C. The elemental analysis corresponds approximately to Li-(Me$_2$NBH$_3$) · 0.5 OC$_4$H$_8$. – C$_8$H$_{26}$B$_2$Li$_2$N$_2$O (201.8): calcd. C 47.00, H 12.88, N 13.87; found C 45.60, H 11.74, N 13.65.

Preparation of Li(CH$_3$)$_2$NBH$_3$ · TMEDA: Me$_2$NH · BH$_3$ (12.37 g, 210 mmol) was dissolved in tetramethylethylenediamine (24.4 g, 31.5 ml, 210 mmol). After cooling of the obtained solution with an ice bath, 150 ml of a 1.56 M LiBu solution in hexane was added with vigorous stirring within a period of 1 h. Stirring was then continued at ambient temp. for 2 more h. Addition of 50 ml of hexane to the suspension resulted in an almost clear solution. Small amounts of insoluble material were removed by filtration. Clear crystals separated from the solution within 12 h (some of them were suitable for an X-ray structure analysis). Cooling of the supernatant solution to –18°C increased the yield to a total of 34 g (90%). – C$_8$H$_{25}$BLiN$_3$ (181.1): calcd. C 53.07, H 13.92, N 23.21; found C 51.99, H 13.39, N 21.84.

Preparation of Li[(CH$_3$)$_2$NBH$_3$] · 0.5 Dioxane: Prepared analogously to 1 · TMEDA from Me$_2$NH · BH$_3$ (6.2 g, 105 mmol), dioxane (9.5 ml, 105 mmol), and 75 ml of a 1.56 M solution of LiBu in hexane. Li(Me$_2$NBH$_3$) · 0.5 dioxane was crystallised from toluene. Yield: 11.1 g (97%). Single crystals were obtained from toluene solutions. – C$_8$H$_{26}$B$_2$Li$_2$N$_2$O$_2$ (217.8): calcd. C 44.12, H 12.03, N 12.86; found C 43.77, H 11.81, N 11.94.

Preparation of Li(Me$_2$NBH$_3$) · 0.5 1,3-Dioxolane: Compound 1 (1.66 g, 25.6 mmol) was suspended in 150 ml of toluene, and diox-

Table 3. Crystallographic data and information regarding data collection and refinement for the Li(Me$_2$NBH$_3$) solvates. Weighting scheme: $w^{-1} = \sigma^2 F_o^2 + (x \cdot P)^2 + y \cdot P$ with $P = (F_o^2 + 2 F_c^2)/3$. Column 2 = TMEDA adduct; column 3 = dioxane solvate; column 4 = trioxolane solvate; column 5 = dioxolane solvate; column 6 = 12-crown-4 complex

Formula	C$_8$H$_{25}$BLiN$_3$	C$_8$H$_{26}$B$_2$Li$_2$O$_2$N$_2$	C$_5$H$_{15}$BLiNO$_3$	C$_7$H$_{24}$B$_2$Li$_2$N$_2$O$_2$	C$_{10}$H$_{25}$BLiNO$_4$
Mol. mass	181.06	217.80	154.9	203.8	241.1
Cryst.size(mm)	0.35x0.4x0.4	0.2x0.35x0.4	0.12x0.15x0.2	0.3x0.32x0.4	0.2x0.3x0.7
Crystal system	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	P2$_1$/n	P$\bar{1}$	P2$_1$/c	P$\bar{1}$	P2$_1$/n
a (Å)	8.585(4)	8.911(1)	10.356(2)	8.947(3)	8.243(2)
b (Å)	12.583(5)	9.577(2)	9.766(2)	9.270(4)	12.651(2)
c (Å)	12.135(5)	10.615(2)	9.415(1)	9.967(4)	27.840(4)
α (°)	90	77.56(1)	90	80.07(2)	90
β (°)	90.67 (3)	65.27(1)	108.00(1)	65.44(2)	90.46(1)
γ (°)	90	63.37(1)	90	64.41(1)	90
V(Å^3)	1311(1)	735.3(2)	905.6(3)	678.1(5)	2903.1(9)
Z	4	2	4	2	8
ρ calc (Mg/m^3)	0.917	0.984	1.136	0.998	1.103
μ (mm^{-1})	0.053	0.063	0.085	0.064	0.080
F(000)	408	240	336	224	1056
T (K)	213	213	203	213	213
Scan range(°)	1.1	1.5	1.2	1.0	0.82
Scan speed (°/min)	3 - 60	2 - 60	3 - 60	4 - 60	4 - 60
2θ-range (°)	2 - 45	4 - 46	4 - 47	4 - 45	3 - 48
Index range	0<h<9	-8<h<6	-11<h<11	-1<h<9	0<h<9
	-1<k<13	-9<k<10	-10<k<0	-9<k<9	-1<k<14
	-11<l<13	-10<l<11	-1<l<10	-10<l<10	-31<l<31
Refl. collect.	1976	5120	1534	2183	5089
Refl. indep.	1687	1849	1264	1772	4326
Refl. (obs., 4σ)	1392	1173	715	1213	2008
R$_{int}$	0.0235	0.043	0.065	0.059	0.054
No. variables	139	223	145	136	325
Wgt. scheme (x,y)	0.061/0.7238	0.0689/0	0.046/0.0	0.064/0.088	0.116/0.80
GOF	1.157	1.02	1.036	1.046	0.858
R1 (4σ)	0.0516	0.0437	0.0584	0.0519	0.0653
wR2 (F^2)	0.1437	0.1034	0.1074	0.1207	0.1635
Largest resid. (e/Å^3)	0.20	0.19	0.19	0.19	0.38

olane (0.9 ml, 1.28 mmol) was added with stirring. The suspension was heated at reflux. A slightly yellow-coloured solution formed. Then small amounts of insoluble material were removed from the hot solution by filtration. On cooling to ambient temp. crystals formed. The suspension was then reduced in vacuo to about 50 ml and the crystalline solvate isolated by filtration. Additional crystals were obtained by cooling the filtrate to $-14\,^{\circ}C$. Yield: 2.27 g of **1** · 0.5 $O_2C_3H_6$ (44%); m.p. $110\,^{\circ}C$. − $C_7H_{24}B_2Li_2N_2O_2$ (204.0): calcd. C 41.25, H 11.77, N 13.74; found C 41.18, H 12.33, N 13.46.

Preparation of Li(Me₂NBH₃) · 1,3,5-Trioxane: Me_2NH · BH_3 (1.18 g, 20 mmol) and trioxane (1.8 g, 20 mmol) were dissolved in 100 ml of toluene. A solution of LiBu (12.7 ml, 1.56 M, 20 mmol) in hexane was added within 10 min to the stirred solution. A colourless product separated. The suspension was then kept at reflux for 1 h and the solution filtered while it was still hot. On cooling needles separated which were recrystallised from hot toluene. Single crystals were obtained by slowly cooling the remaining solution. Yield: 2.79 g of **1** · $O_3C_3H_6$ (90%), m.p. $64\,^{\circ}C$ (dec.). − $C_5H_{15}BLiNO_3$ (154.9): calcd. C 38.76, H 9.76, N 9.04; found C 37.42, N 9.74, H 8.83.

Preparation of Li(Me₂NBH₃) · 12-Crown-4: Prepared in analogy to **1** · trioxane from Me_2NH · BH_3 (300 mg, 5 mmol), 12-crown-4 (880 mg, 5 mmol), 50 ml of toluene, and LiBu (4.23 ml, 1.57 M, 5 mmol). The complex separated from the solution on cooling as well-formed crystals. Yield: 1.08 g of **1** · 12-crown-4 (90%), m.p. $90\,^{\circ}C$ (dec.). − $C_{10}H_{25}BLiNO_4$ (241.1): calcd. C 49.82, H 10.45, Li 2.88, N 5.81; found C 50.11, H 9.17, Li 2.53, N 4.08.

X-Ray Structure Determinations: Single crystals were mounted in glass capillaries in perfluoroether oil. Crystal alignment, centreing of reflections and data collection were performed at 213 K by using the LT device for the Siemens P4 diffractometer with graphite-monochromated $Mo\text{-}K_\alpha$ radiation. Lorentz and polarisation correction was applied in data reduction. The SHELXL Plus programme[15] was used for structure solution by direct methods while the SHELXL 93-PC[15] programme was used for all other calcu-

lations. Nonhydrogen atoms were refined anisotropically. Positional parameters of boron bound hydrogen atoms were refined freely with fixed U_{iso} values. All other hydrogen atom positions were calculated (although most of them were detected in difference Fourier synthesis) and included in the final refinement with a riding model and fixed $U_{iso,H}$ = 1.2 $U_{eq,C}$. Graphical display used the XP programme[15]. Relevant data are summarised in Table 3. Further details on the crystal structure determinations are available at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-404646, -404715 to -404719, the names of the authors, and the journal citation.

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