Synthesis and Structures of $LiBH_4$ Complexes with *N*-Heterocycles [1]

Stefanie Leiner, Peter Mayer, and Heinrich Nöth

Department Chemie und Biochemie, Universität München, Butenandtstr. 5 – 13, Haus D,
81377 München, Germany

Reprint requests to Prof. Dr. H. Nöth. E-mail: H.Noeth@lrz.uni-muenchen.de

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$LiBH_4$ solutions in diethyl ether or tetrahydrofuran react with *N*-methylmorpholine, *N*-methylimidazole or piperidine not only with the formation of adducts $LiBH_4(L)_n$ (n = 1 or 3) but also with formation of amine boranes $BH_3(L)$. While $LiBH_4$ and *N*-methylimidazole form the 1 : 3 adduct **1**, *N*-methylmorpholine produces the 1 : 1 adduct **2**. In both cases the adducts contain hexacoordinated Li atoms. In **1** the Li atom is coordinated to three N atoms and three H atoms. However, in compound **2** the molecules are connected in the solid state with one another to form a two-dimensional polymer built from dimeric units $(LiBH_4)_2$ that are connected to adjacent dimeric units *via* the O and N atoms of the *N*-methylmorpholine ligand. Each of the Li atoms in **2** is connected to four H atoms *via* Li–H–B hydrogen bridges and an O and an N atom. The reaction of $LiBH_4$ with piperidine leads to the compound $(LiBH_4)_6(HNC_5H_{10})_{16}$, **3**, which consists of two independent $LiBH_4(HNC_5H_{10})_3$ molecules and two others of composition $(LiBH_4)_2(HNC_5H_{10})_5$ containing penta- and hexacoordinated Li atoms.

Key words: Lithium Tetrahydridoborate Complexes, *N*-Methylmorpholine, *N*-Methylimidazole, Piperidine, X-Ray Crystal Structure Determination

Introduction

The structure of alkali metal tetrahydroborate complexes with ethers or amines varies considerably, depending a) on the size of the alkali metal ion and b) on the type and number of the ether or amine ligands. The BH_4 group supplies up to four of its hydrogen atoms for coordination to the alkali metal atoms. The following bonding types are known: M(HB) ($\mu_1{}^1$-type), $M(H_2B)$ ($2\mu_1{}^1$-type), $M(H_3B)$ ($3\mu_1{}^1$-type), M(HB)M ($\mu_2{}^2$-type), $M(HB)_2M$ ($2\mu_2{}^2$-type), or $M(HB)M_2$ ($\mu_3{}^3$-type) (superscripts denote the number of M atoms to which one H atom is coordinated, subscripts show the coordination number of the H atoms involved in the bridging function). For mononuclear $LiBH_4$ complexes the coordination number of the Li atoms is either 5 or 6, but may also be 7. The coordination number of the Na atoms in complexes $NaBH_4(L)_n$ can be 6, but may increase to 7, 8 and even 9. So far, only the structures of a few KBH_4 complexes have been determined, and in crown ether complexes the cations show coordination numbers up to 8 [1]. If the number of ligands bonded to the alkali metal atoms decreases, then the MBH_4 complexes become dimeric, trimeric or even polymeric. In these cases the hydrogen atoms of the BH_4 groups bridge two, three or even four alkali metal centers [1]. Bifunctional cyclic ligands such as dioxane, dioxolane or morpholine and others prefer the formation of polymeric MBH_4 solvates (M = Li, Na), as has been demonstrated for $NaBH_4$(morpholine)$_2$ [1] which consists of three-dimensionally interconnected molecules with hexa-, hepta- and even octa-coordinated Na centers. We recently investigated the coordination of $LiBH_4$ with *N*-methylimidazole and *N*-methylmorpholine and include here also a $LiBH_4$ adduct of piperidine.

Results

Synthesis

It is well known that amine complexes of $LiBH_4$ can be readily prepared from their components in diethyl ether solutions according to Eq. 1. However, we have also observed that the reactions with *N*-morpholine and *N*-methylimidazole can lead to the formation of the respective amine-borane adduct. For instance, the 1 : 1 and the 1 : 3 reaction of *N*-methylimidazole with $LiBH_4$ in diethyl ether led to insoluble $LiBH_4(MeN_2C_3H_3)_3$, **1**, and soluble $H_3B(MeN_2C_3H_3)$, while the reaction in THF generated only **1**, irrespective of the molar ratio of the reactants. The same behavior was observed in reactions of $LiBH_4$ with *N*-methylmorpholine. Here, the borane adduct H_3B-

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($MeNC_4H_8O$) (≈70 %) was the main reaction product when the reaction was performed in diethyl ether solution and in a 1 : 3 molar ratio.

$$\underset{}{LiBH_4(OEt_2)} + n\mathrm{L} \rightarrow \underset{\mathbf{1,2,3}}{LiBH_4(L)_n} + OEt_2 \qquad (1)$$

1: $n = 3$, L = *N*-methylimidazole
2: $n = 1$, L = *N*-methylmorpholine
3: $n = 2.66$, L = piperidine

$$LiBH_4(OEt_2) + L \rightarrow LiH + BH_3(L) \qquad (2)$$

The 1 : 1 addition product of $LiBH_4$ with *N*-methylimidazole could not be crystallized in contrast to compound **2**. Compound **3** which separated from a $LiBH_4$ solution in piperidine after addition of methylcyclohexane, has an unexpected 6 : 16 Li : L ratio. Its crystal structure study proved it to consist of a mixture of two molecules of $LiBH_4(HNC_5H_{10})_3$ with two molecules of $(LiBH_4)_2(HNC_5H_{10})_5$. It is interesting to note that the LiH formed according to Eq. 2 does not form a mixed complex with the $LiBH_4$ solvates.

As expected, compounds **1**–**3** show 1 : 4 : 6 : 4 : 1 quintets in the ^1H-coupled ^{11}B NMR spectra, *viz.* at $\delta^{11}B = -41.7$ ppm, $^1J(^1H^{11}B) = 79$ Hz for **1**, $\delta^{11}B = -40.7$ ppm, $^1J(^1H^{11}B) = 80$ Hz for **2**, and $\delta^{11}B = -41.6$ ppm, $^1J(^1H^{11}B) = 82$ Hz for **3**. The corresponding amine-BH_3 adducts are characterized by 1 : 3 : 3 : 1 quartets at $\delta^{11}B = -19.1$ ppm, $^1J(^1H^{11}B) = 97$ Hz for $H_3B(MeN_2C_3H_3)$, and $\delta^{11}B = -10.9$ ppm, $^1J(^1H^{11}B) = 97$ Hz for $H_3B(MeNC_4H_8O)$. The ^7Li NMR signal of the 1 : 1 reaction product of $LiBH_4$ with *N*-methylimidazole in THF shows a singlet at $\delta = -1.25$ ppm, and for the 1 : 3 reaction product a singlet at $\delta = 0.46$ ppm. This indicates that the products are solvated differently by THF. In contrast, the products obtained from $LiBH_4$ and *N*-methylmorpholine in the 1 : 1 and 1 : 3 ratio both show a single ^7Li NMR signal at $\delta = -0.42$ ppm in THF. Because only **2** could be isolated, it is evident that the THF solvate is the same in both cases.

Three sharp and intense IR bands are observed for compound **1** at 2360, 2306 and 2269 cm^{-1} corresponding to $\nu(BH_{terminal})$, $\nu(BH_{3,asym})$, and $\nu(BH_{3,sym})$, respectively, while there are four BH bands in the IR spectrum of compound **2**. These latter four bands are rather broad (4 maxima at 2356, 2321, 2301, and 2259 cm^{-1}) and show clearly that the BH_4 groups of **2** are interacting differently with the Li atoms of compound **1** as shown by their crystal structures.

X-Ray structures

Compound **1** crystallizes in the monoclinic system, space group *Cc*, $Z = 4$. The structure of the molecule $LiBH_4$(*N*-methylimidazole)$_3$ is shown in Fig. 1. Its Li atom is hexacoordinated, and the BH_4 group binds to the Li atom with three of its H atoms. For this reason the B1–Li1 distance is rather short at 2.389(4) Å. However, the BH_4 group binds asymmetrically to the Li atom as shown by two short [2.17(5) and 2.17(5) Å] and one slightly longer Li–H bridge distances [2.21(7) Å]. This asymmetry is also demonstrated by N–Li–H bond angles which range from 92(2) to 142(1)°. On the other hand, the N–Li–B angles are close to the tetrahedral angle, ranging from 102.8(2) to 115.1(2)°, while the H–B–H bond angles deviate even more, as shown by the H1B–B1–H1D and H1A–B1–H1C bond angles of 104(3)° and 116(3)°. The B–H bond lengths vary from 1.03(5) to 1.11(4) Å,

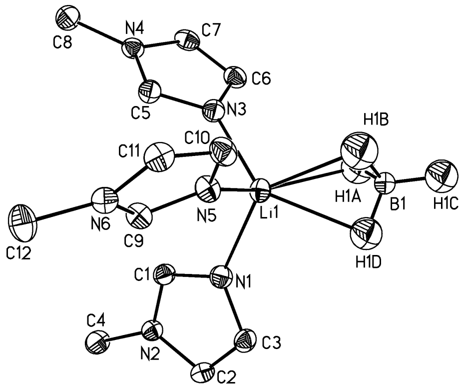

Fig. 1. The molecular structure of $LiBH_4$-tris-*N*-methylimidazol, **1**. Thermal ellipsoids represent 25 % probability. Selected bond lengths (Å) and angles (deg): Li1–N1 2.094(4), Li1–N5 2.072(4), Li1–N3 2.101(4), Li1–B1 2.381(4), Li1–H1A 2.21(3), Li1–H1B 2.17(4), Li1–H1C 2.17(5), B1–H1A 1.05(4), B1–H1B 1.11(4), B1–H1C 1.08(4), B1–H1D 1.03(5), N1–C1 1.314(3), N1–C3 1.375(3), N2–C1 1.343(3), N2–C2 1.365(3), N2–C4 1.461(3), N3–C5 1.317(3), N3–C6 1.366(3), N4–C5 1.342(3), N4–C7 1.364(3), N4–C8 1.467(3), N5–C11 1.376(3), N6–C9 1.346(3), N6–C11 1.364(3), N6–C12 1.458(3), C2–C3 1.352(3), C6–C7 1.360(3), C10–C11 1.357(3); N1–Li1–N5 104.5(2), N1–Li–N3 102.9(2), N3–Li1–N5 103.5(2), N1–Li1–B1 115.1(2), N3–Li1–B1 113.9(2), N5–Li1–B1 115.15(2), N1–Li1–H1A 95(1), N3–Li1–H1a 105.8(9), N5–Li1–H1A 141(1), N1–L1–H1B 140(1), N3–Li1–H1B 92(1), N6–Li1–H1B 108(1), N1–Li1–H1D 114(1) N3–Li1–H1D 137(1), N5–Li1–H1D 95(1), N3–Li1–H1B 108(1), N3–Li1–H1D 137(1), H1A–Li1–H1D 47(2), H1B–Li1–H1D 45(2), H1A–B1–H1B 106(3), H1A–B1–H1C 116(3), H1A–B1–H12D 105(3), H1B–B1–H1C 108(3), H1B–B1–H1D 104(3), H1C–B1–H1D 116(3).

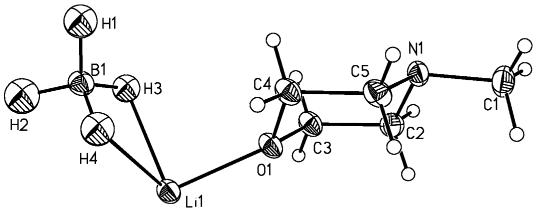

Fig. 2. The asymmetric unit of $LiBH_4$-*N*-methylmorpholine, **2**. Selected bond lengths (Å) and angles (deg), Li* denotes the atom in the polymeric array: Li1–O1 1.982(2), Li1*–N1 2.181(2), O1–C3 1.438(2), O1–C4 1.437(2), N1–C2 1.470(2), N1–C5 1.475(2), N1–C1 1.474(2), Li1–B1 2.457(3), Li1–H4 1.96(2), Li1–H3 2.06(2), B1–H1 0.99(2), B1–H2 1.14(2), B1–H3 1.16(2), B1–H4 1.15(2); C3–O1–C4 109.15(9), C2–N1–C5 108.5(1). C5–N1–C1 109.5(1), C2–N1–C1 108.5(1), O1–Li1–B1 102.8(9), H4–Li1–H3 54.4(7), H4–B1–H3 106(1), H1–B1–H2 109(1).

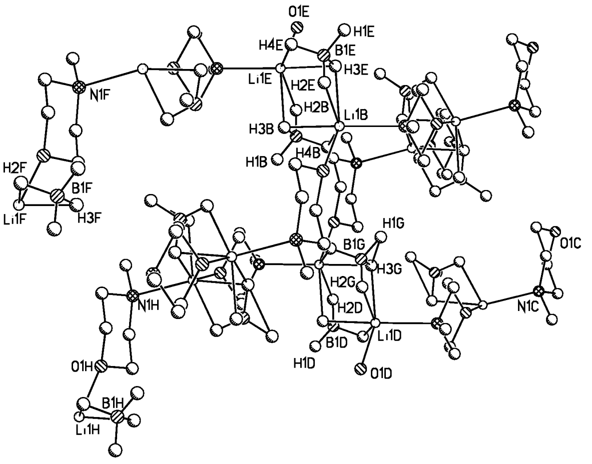

Fig. 3. Connectivity pattern of the molecules of **2** in the crystal generating a two-dimensional array with hexacoordinated Li atoms. Only two strings are shown. The four H atoms of two adjacent BH_4 groups form one terminal H atom, the remaining three H atoms are involved in one $\mu_2{}^2$ and two $\mu_2{}^1$ bridges. The chains are interconnected *via* Li–O and Li–N bonds.

i. e. they can be considered to be of equal lengths within the limits of the 3σ criterion. The shortest distance of 1.03(5) Å is to atom H1D which interacts only weakly with Li1, while the terminal H1C atom shows a B–H bond length of 1.08(4) Å.

The structure of solid $LiBH_4$-*N*-methylmorpholine, **2**, differs considerably from the structure of **1**. The compound crystallizes in the monoclinic system, space group *P*2/c, *Z* = 4. Fig. 2 shows the molecule in the asymmetric unit which consists of an *N*-methylmorpholine unit added to a $LiBH_4$ molecule. Its tricoordinated Li atom is coordinatively unsaturated. Therefore,

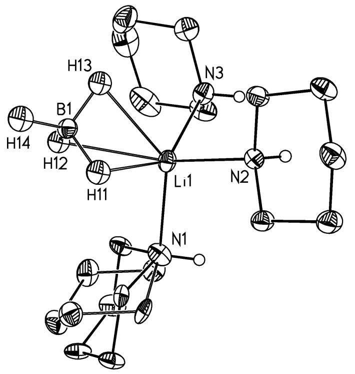

Fig. 4. Molecular structure of the first independent $LiBH_4(HNC_5H_{10})_3$ unit in **3** showing the disordered piperidine unit. Selected bond lengths (Å) and angles (deg): Li1–N1 2.156(8), Li1–N2 2.169(7), Li1–N3 2.205(6), Li1–B1 2.387(7), Li1–H11 2.07(4), Li1–H12 2.30(4), Li1–H13 2.36(4), B1–H11 1.15(4), B1–H12 1.18(5), B1–H13 1.12(5), B1–H14 1.10(4); N1–Li1–N2 107.5(3), N1–Li1–N3 113.9(3), N2–Li1–N3 95.1(3), H11–Li1–H12 51(1), H11–Li1–H13 48(1), H11–B1–H12 108(3), H11–B1–H13 107(3), H11–B1–H14 110(3), H12–B1–H13 107(3), H12–B1–H14 114(3), H13–B1–H14 109(3).

these units associate in the solid state. Fig. 3 shows the two-dimensional arrangement of these units where the $LiBH_4$ units become dimeric, and these dimeric $LiBH_4$ molecules are connected by the N and O atoms of the *N*-methylmorpholine molecules. This results in hexacoordinated Li atoms. Each BH_4 group of the $(LiBH_4)_2$ dimers shows a terminal BH bond. Another hydrogen atom is involved in forming an Li–H–Li bridge, while the other two H atoms of each BH_4 group bind to only one Li atom in a $2\mu_2{}^1$ manner, *i. e.* by two single bridge bonds. The B–H bond lengths range from 1.14(2) to 1.16(2) Å. The longest bonds result for the H3 and H4 atom which bind to two Li atoms. These two Li–H bonds are 1.96(2) and 2.06(2) Å long, the Li–B distances are 2.457(3) and 2.467(3) Å, and the Li–Li distance is 3.081(4) Å.

The product obtained from $LiBH_4$ and piperidine has the unusual composition $(LiBH_4)_6(pip)_{16}$, **3**. In the asymmetric unit of the triclinic system, space group $P\bar{1}$, there are actually four different molecules, two with the composition $LiBH_4(pip)_3$ and two with the composition $(LiBH_4)_2(pip)_5$. These are shown in Figs. 4 to 7. The first two molecules of the type $LiBH_4(pip)_3$ (Figs. 4 and 5) differ in so far as the molecule shown in Fig. 4 contains only a distorted hexacoordinated Li1 atom, *i. e* the BH_4 group forms three Li–H–B bridge bonds *via* atoms H11, H12 and H13 with Li–H bond lengths of 2.07(4), 2.30(4) and

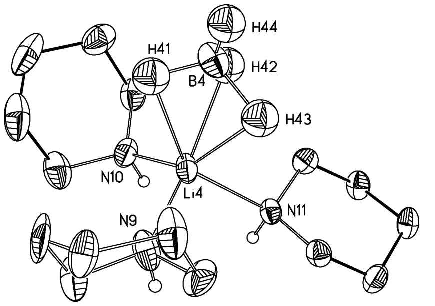

Fig. 5. The molecular structure of the second independent $LiBH_4(HNC_5H_{10})_3$ unit in **3**. Only one orientation of the disordered piperidine group at atom N9 is shown. Seleced bond lengths (Å) and angles (deg): Li4–N9 2.150(8), Li4–N10 2.217(8), Li4–N11 2.181(8), Li4–B4 2.416(8), Li4–H41 2.27(5), Li4–H42 2.16(5), Li4–H43 2.11(6), B4–H41 1.20(5), B4–H42 0.87(9), B4–H43 1.40(7), B4–H44 1.04(7); N9–Li4–N10 114.1(3), N9–Li4–N11 106.3(3), N10–Li4–N11 96.9(3), N9–Li4–B4 109.8(3), H41–Li4–H42 46(2), H41–Li4–H43 59(2), H42–Li4–H43 53(3), H41–B4–H42 112(6), H41–B4–H43 113(3), H41–B4–H44 106(4), H42–B4–H43 86(6), H42–B4–H44 131(6), H43–B4–H44 107(4).

2.36 Å. The corresponding B–H bond lengths are 1.15(4), 1.18(5), and 1.12(4) Å while the B–H bond length to the terminal H14 atom is slightly shorter with 1.10(4) Å. In accord with this is the B1–Li1 distance of 2.387(7) Å. One of the three chair-shaped piperidine rings (see Fig. 4) is site disordered. The Li1–N bonds to atoms N1, N2 and N3 are 2.156(8), 2.169(7) and 2.205(6) Å, respectively, and the N–Li–N bond angles of 107.5(3) (N1–Li1–N2), 113.9(3) (N1–Li1–N3) and 95.1(3)° (N2–Li1–N3) are quite different. As a consequence, the N–Li1–B1 bond angles are also not equal with N1–Li1–B1 111.44(3), N2–Li1–B1 112.22(3) and N3–Li1–B1 115.4(3)°. They are much closer together than the N–Li–N bond angles. Nevertheless, the N_3LiB unit can best be described as a distorted tetrahedral array rather than a distorted pentagonal bipyramid because the H–Li1–H bond angle is only 46.6(5)°.

The second molecule of composition $LiBH_4$-$(HNC_5H_{10})_3$ (Fig. 5) contains no disordered piperidine molecules, and the coordination number for Li4 is six and not five as for Li1, because its BH_4 group is attached to the Li4 atom by three $\mu_2{}^1$ bridges, although the hydrogen atoms are asymmetricallly bonded to the Li4 center, as shown by Li–H bond lengths of 2.27(5), 2.16(5), and 2.11(6) Å. On the other hand, the Li4–B4 distance is 2.416(8) Å, *i. e.* longer than the Li1–B1 distance. This finding is against the rule that the B–Li distances become shorter if one moves from Li–H–B bridges *via* $Li(H_2)B$ to $Li(H_3)B$ bridge bonds [2]. The three N–Li4–N bond angles are 114.1(3) (N9–Li4–N10), 106.3(3) (N9–Li4–N11) and 96.9(3)° (N10–Li4–N11), similar to those at atom Li1.

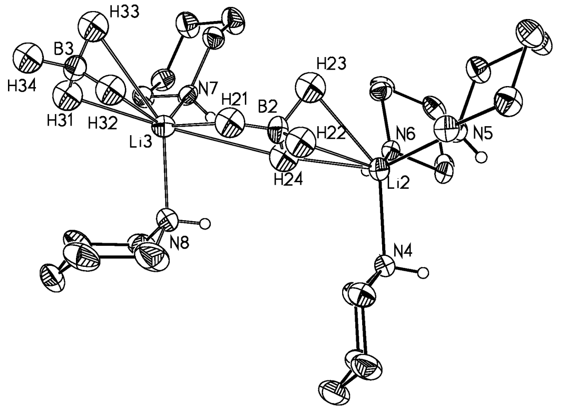

Fig. 6. Molecular structure of the first independent $(LiBH_4)_2$-$(HNC_5H_{10})_5$ unit in **3**. Bond lengths (Å) and bond angles (deg): Li2–N4 2.110(8), Li2–N5 2.119(6), Li2–N6 2.102(6), Li3–N7 2.036(7), Li3–N8 2.108(8), Li2–B2 2.438(8), Li3–B2 2.772(8), Li3–B3 2.409(8), Li2–H22 2.28(4), Li2–H24 2.12(4), Li3–H21 2.04(5), Li3–H31 2.21(5), Li3–H32 2.01(4), B2–H21 1.07(6), B2–H22 0.98(6), B2–H23 1.17(6), B2–H24 1.06(4), B3–H31 1.04(5), B3–H32 1.15(4), B3–H33 1.08(6), B3–H34 1.16(4); N4–Li2–N5 106.9(3), N4–Li2–N6 105.9(3), N5–Li2–N6 109.4(3), N7–Li3–N8 104.9(3), N8–Li3–B2 125.6(3), N4–Li2–B2 111.8(3), N5–Li2–B2 113.4(3), N6–Li2–B2 109.2(3), H22–Li2–H24 46(2), H31–Li3–H32 79(2), H31–Li3–H32 51(2), H21–Li3–H31 130(2), H21–B2–H22 109(4), H21–B2–H23 116(4), H21–B2–H24 113(3), H22–B2–H23 90(4), H22–B2–H24 117(4), H23–B2–H24 106(3), H31–B3–H32 113(4), H31–B3–H33 106(4), H31–B3–H34 112(3), H32–B3–H33 110(4), H32–B3–H34 106(3), H33–B3–H34 111(4).

In addition to these two units there are two independent dinuclear species of composition $(LiBH_4)_2$-$(HNC_5H_{10})_5$ in the unit cell. The molecular structures of these two molecules are depicted in Figs. 6 and 7. A typical feature is that the Li atoms Li2 and Li3 are hexacoordinated (Fig. 6) while atoms Li5 and Li6 (Fig. 7) are pentacoordinated. The latter form two Li–H–B bridge bonds with the $(B6)H_4$ group and a single Li(6)–H(52)–B(5) bridge bond of 121(3)°. In contrast, Li(3) shows $2\mu_1{}^1$ H hydrogen bridges to atom B3 while atom H24 bridges to Li2 and Li3. H21 binds to Li3, but H22 and H23 form bridges to Li2. This has the following consequences for the Li–B distances: 2.438(8) for Li2–B2, 2.772(8) Å for Li3–B2 and 2.409(8) Å for Li3–B3. The Li6–B5 distance is 2.670(9) Å, and 2.452(7) Å are found for Li6–B6. It

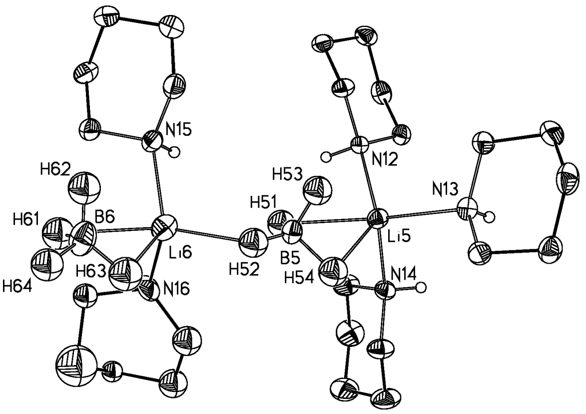

Fig. 7. The second independent $(LiBH_4)_2(HNC_5H_{10})_5$ unit in **3**. Only one site-disordered piperidine ring (C76A to C80A at the N16 atom) is shown. Selected bond lengths (Å) and bond angles (deg): Li5–N12 2.098(7), Li5–N13 2.121(7), Li5–N14 2.131(6), Li6–N15 2.035(7), Li6–N16 2.065(7), Li5–B5 2.443(7), Li6–B5 2.670(8), Li6–B6 2.452(7), Li5–H51 2.19(4), Li5–H54 2.16(5), Li6–H52 2.00(5), Li6–H51 2.63(6), Li6–H61 2.30(5), Li6–H62 2.67(5), Li6–H63 2.02(5), B5–H51 1.04(4), B5–H52 1.02(5), B5–H53 1.07(7), B5–H54 1.19(5), B6–H61 1.15(5), B6–H62 1.10(8), B6–H63 1.10(5), B6–H64 1.18(6); H51–Li5–H54 49(2), H51–Li5–H53 43(2), H52–Li6–H61 133(2), H52–Li6–H63 87(2), H61–Li6–H63 48(2), H51–B5–H52 116(4), H51–B5–H53 108(4), H51–B5–H54 106(3), H52–B5–H53 110(3), H53–B5–H54 102(4), H61–B6–H62 96(5), H61–B6–H63 103(5), H61–B6–H64 116(3), H62–B6–H63 129(5), H62–B6–H64 107(5), H63–B6–H64 106(3).

is somewhat surprising that the Li–N bond lengths, and particularly the N–Li–N bond angles of the two types of Li atoms are almost the same. This, for example, is shown by the Li–N bond lengths to atom Li2 which are 2.110(8), 2.119(6) and 2.102(6) Å, while to atom Li3 the Li–N bond lengths are 2.036(7) and 2.108(8) Å. The N–Li2–N bond angles are 106.9(3), 105.9(3) and 109.4(3)° similar to the N–Li3–N bond angles of 104.9(3), 106.0(3) and 109.1(3)°. While the N–Li2–B2 bond angles are close to 110° [N4–Li2–B2 111.8(3), N5–Li2–B2 113.3(3), N6–Li2–B2 109.3(3)°] the N–Li3–B3 bond angles are different, as shown by 109.7(3)° for N7–Li3–B3 and 125.7(3)° for N8–Li3–B3. The piperidine ring of atom N10 is site-disordered, *i. e.* out of the 15 piperidine rings in the four molecules three of them show disorder.

Discussion

Amine solvates of $LiBH_4$ very often have the composition $LiBH_4(L)_3$. In most of these compounds the Li center is hexacoordinated by three Li–N and three Li–H bonds. This leads to short Li–B distances as the Li atom is centered more or less accurately below a trigonal plane of the BH_4 group [2]. Compound **1** belongs to this class of compounds. In general, $LiBH_4$ coordination compounds of amines having the composition $LiBH_4(L)_2$ are dimeric. In this case the two Li atoms are usually hexacoordinated by two N and four H atoms. This results from two Li–H(B)–Li bonds in which the H atoms are tricoordinated ($\mu_3{}^2$-type), and two Li–H–B bonds from each BH_4 group. This leaves one H atom of each BH_4 unit uncoordinated. Typical examples are $[LiBH_4(2\text{-Mepy})]_2$ [1], $[LiBH_4(TMEDA)]_2$ [3], $[LiBH_4(HNbzl_2)]_2$ [4], or $[LiBH_4(bzlNCH_2)_3]$ [5]. Finally, compounds of composition $LiBH_4(L)$ are either forming two-dimensional or even three-dimensional arrays in the solid state where up to all four hydrogen atoms are building either LiH_2BH_2Li, LiH_3BHLi, LiH(B)HLi, or $LiH(BH)_2Li_2$ bridges [6] in order to be coordinatively saturated. Usually lithium is present in a hexa-coordinated state, but also penta- and heptacoordination is observed [1, 5]. The coordination of $LiBH_4$ units with heterocycles having two basic sites for coordination leads in general to cross-linking, as has been reported for the ligands dioxane and dioxolane [5], and here we show that *N*-methylmorpholine, as demonstrated for compound **2**, is no exception. A two-dimensional structure is generated containing hexacoordinated Li atoms. Its structure is, however, totally different compared with $NaBH_4$(*N*-methylmorpholine) [1], which shows a three-dimensional array of atoms with hexa- and heptacoordinated Na atoms.

Generally, primary and secondary amines react with $LiBH_4$ to generate 1 : 3 or 1 : 2 compounds. However, it was observed that *tert*-$BuNH_2$ reacts with $LiBH_4$ to generate the compound $(LiBH_4)_3(H_2N\textit{tert}\text{-Bu})_4$ which has a linear polymeric structure in the solid state [1]. Triorganyltriazanes react with $LiBH_4$ even with formation of $[Li(triazane)_2][Li(BH_4)_3]$ salts [5]. So, the piperidine complex **3** reported here is an exception as far as its composition and structure is concerned, because it contains not only the classical unit $LiBH_4(L)_3$ but also a $LiBH_4(L_2)$ unit which is connected to the $LiBH_4(L)_3$ fragment by a single Li–H–B bridge bond generating binuclear molecules $(LiBH_4)_2(HNC_5H_{10})_5$. This result shows that further studies may reveal new structural types of coordination compounds, not only of $LiBH_4$ but also of the other alkali metal tetrahydroborates.

Experimental Section

All experiments were performed under anhydrous conditions using Schlenk techniques in an atmosphere of dry nitrogen gas and anhydrous solvents. The amines used were bought from Aldrich Chemicals Corp. $LiBH_4$ was supplied by Chemetall Corp. Saturated solutions in ethers were prepared by using diethyl ether and tetrahydrofuran. NMR: Jeol 400, THF solutions; solutions of $BF_3{\cdot}OEt_2$ or 1 M aqueous LiCl as external standards. IR: Perkin-Elmer 883 in Hostaflon/Nujol. Elemental analysis was performed in the microanalytical laboratory of the department. X-Ray structure determination: Bruker P4 diffractometer equipped with an area detetector for compound **3**, or a kappa 4 instrument with a rotating anode and an area detector for compounds **1** and **2**.

Lithium tetrahydridoborate tris(N-methylimidazole), ***1***

1 : 1 Reaction in diethyl ether: *N*-Methylimidazole (0.63 mL, 8.0 mmol) was dissolved in diethyl ether (20 mL). To the stirred solution was added a 0.8 M solution of $LiBH_4$ (10 mL). A white precipitate formed rapidly. It was isolated by filtration after 2 h stirring, washed with diethyl ether and dried *in vacuo*. The filtrate showed a quartet at $\delta^{11}B = -18.4$ ppm, $^1J(^{11}B^1H)$ 97.5 Hz for compound $H_3B(MeN_2C_3H_3)$. The insoluble product was dissolved in THF. This solution showed a small ^{11}B NMR signal at $\delta = -19.1$ ppm, $^1J(^{11}B^1H) = 97.5$ Hz, and a dominating signal at $\delta^{11}B = -41.74$ ppm (quintet, $^1J(^{11}B^1H) = 79$ Hz). Yield of **1**: 0.67 g (31 %).

1 : 3 Reaction in diethyl ether: *N*-Methylimidazole (1.90 mL, 24 mmol) was dissolved in diethyl ether (20 mL) and added while stirring to a solution of $LiBH_4$ in diethyl ether (10 mL, 0.8 M solution). A solid that formed rapidly was isolated by filtration, washed with diethyl ether (20 mL) and dried *in vacuo*. Yield: 1.6 g of **1** (74.7 %), m. p. 99 °C, dec. A solidified part melted at around 230 °C. – NMR: ^{11}B (THF): $\delta = -41.6$ ppm, quint. $^1J(^{11}B^1H) = 80$ Hz. – ^7Li NMR (THF): $\delta = -0.99$, s. – $C_{12}H_{66}N_6BLi$ (268.1): calcd. C 53.76, H 8.27, N 31.35; found C 53.36, H 7.90, N 30.78.

1 : 1 Reaction in THF: *N*-Methylimidazole (0.57 mL, 7.2 mmol) was dissolved in THF (15 mL), and a THF solution of $LiBH_4$ (10 mL, 0.72 M) was added with stirring. A slightly turbid solution resulted. – NMR: ^{11}B NMR (THF): $\delta = -41.3$ ppm, quintet, $^1J(^{11}B^1H) = 80.5$ Hz. – ^7Li NMR (THF): $\delta = 0.11$, s.

1 : 3 Reaction in THF: To a solution of *N*-methylimidazole (1.71 mL, 21.6 mmol) in THF (15 mL) was added a $LiBH_4$ solution in THF (10 mL, 0.72 M). A white solid precipitated which was isolated by filtration after 3 h. It was dried, washed with some THF, and dried again. Colorless crystals of rhombic habitus separated form the filtrate. The filtrate showed only the presence of a $LiBH_4$ solvate. – ^{11}B NMR (THF): $\delta = -41.5$, quint., $^1J(^{11}B^1H) = 76.3$ Hz. – ^7Li NMR: $\delta = -0.46$, s. – $C_{12}H_{66}N_6BLi$ (268.1): calcd. C 53.76, H 8.27, N 31.35; found; C 53.21, H 8.16, N 30.94.

Lithium tetrahydridoborate N-methylmorpholine, ***2***

1 : 1 Reaction in diethyl ether: *N*-Methylmorpholine (0.88 ml, 7.2 mmol) was dissolved in diethyl ether (20 mL). To the stirred solution was added a 0.72 M solution of $LiBH_4$ in THF (10 mL). A white precipitate formed rapidly. 2 h after addition of the morpholine the solid was isolated by filtration, washed twice with diethyl ether and dried *in vacuo*. The filtrate showed in the ^{11}B NMR spectrum signals at $\delta = -11.96$, quart., $^1J(^{11}B^1H) = 101.$ 9 Hz and -42.77 quint., $^1J(^{11}B^1H) = 81$ Hz (ratio : 7 : 3). – ^7Li NMR: $\delta = -1.50$. Yield of solid: 0.50 g (51 %), m. p. 250 °C. – $C_5H_{15}ONBLi$ (122.9); calcd. C 48.84, H 12.30, N 11.39; found C 48.47, H 12.48, N 11.31.

Lithium tetrahydridoborate piperidine complex ***3***

$LiBH_4$ (215 mg, 9.87 mmol) was added to stirred piperidine (20 mL) where it dissolved. Then methylcyclohexane (4 mL) was added and the mixture cooled to 8 °C. Within a few hours colorless crystals of rhombic habitus separated. These were isolated by filtration and washed with methylcyclohexane and then with pentane. Yield: 368 mg (15 %), m. p. 68 – 79 °C (dec.). – ^{11}B NMR (piperidine): $\delta = -41.6$, quint., $^1J(^{11}B^1H) = 82$ Hz. – IR (Nujol/Hostaflon, cm^{-1}): $\nu = 2329$ (sh), 2252 st, 2184 (sh), for the BH_4 group, broad signals. – $C_{80}H_{200}N_{16}B_6Li_6$ (1493.8): calcd. C 74.36, H 13.50, N 15.01; found C 72.13, H 13.25, N 14.31.

X-Ray structure determinations

Crystals were selected under the cover of nitrogen gas from a suspension in cold poly-perfluoroether oil. The dimensions of the unit cells were determined from all data collected in the hemisphere mode. Data were reduced with the programm SAINT [7], and the structure was solved with the programme package SHELX-97 [8]. Several single crystals of compound **3** were investigated as they turned out to be twinned. Data of the species that was suitable for the structure determination lead to an internal *R* value of 0.037. Nevertheless, three of the 15 piperidine ligands (attached to Li1, Li2, and Li4) showed site disorder. The occupancy factor for the site-disordered chair rings in **3** were close to 0.5 for those at N3 and N5, but 0.6 and 0.4 for those at N10. In the final refinement they were fixed to these values. The C–C bonds of these piperidine rings were set at a fixed value of 1.54 Å with a standard deviation of 0.08 because with no constraints the C–C bonds varied from 1.32 to 1.77 Å. The isotropic displacement parameters for these carbon atoms spanned the range from 0.06 to 0.08. For this reason they were refined in

	1	**2**	**3**
Chem. formula	$C_{12}H_{22}N_6BLi$	$C_5H_{15}NOBLi$	$C_{12}H_{122}N_{16}B_6\,Li_6$
Form. wght.	268.1	122.93	1492.05
Cryst. size, mm^3	$0.41 \times 0.18 \times 0.14$	$0.41 \times 0.18 \times 0.14$	$0.4 \times 0.3 \times 0.2$
Cryst. system	monoclinic	monoclinic	triclinic
Space group	*Cc*	$P2_1/c$	$P\bar{1}$
a, Å	13.334(3)	11.069(2)	11.1071(7)
b, Å	9.261(2)	7.671(2)	20.902(1)
c, Å	13.063(3)	11.139(2)	22.858(2)
α, deg	90	90	79.009(1)
β, deg	91.61(3)	116.92(3)	89.651(1)
γ, deg	90	90	81.651(1)
V, Å3	1612.4(6)	843.3(3)	5150.8(6)
Z	4	4	2
$\rho_{\text{calcd.}}$, mg m^{-3}	1.104	0.968	0.962
$\mu(\text{Mo}K_\alpha)$, cm^{-1}	0.069	0.061	0.055
$F(000)$, e	576	272	1678
Index range *hkl*	$-17 \le h \le 16$	$-14 \le h \le 14$	$-12 \le h \le 12$
	$-12 \le k \le 12$	$-9 \le k \le 9$	$-22 \le k \le 22$
	$-16 \le l \le 16$	$-14 \le l \le 13$	$-25 \le l \le 25$
$2\theta_{\text{max}}$, deg.	54.96	54.96	46.52
T, K	193(2)	193(2)	188(2)
Refl. coll./unique	6536/3575	6422/1912	23029/11847
R_{int}	0.0335	0.0324	0.0372
Refl. observed (2σ)	3123	1535	7315
No. ref. variables	229	142	1176
Final $R1^a$ (4σ)	0.03340	0.0440	0.0702
Final $wR2^a$	0.0939	0.1318	0.1847
Weight. scheme^a *x/y*	0.0757/0.436	0.0641/−0.1221	0.1134/1.4653
GoF^b	0.912	1.117	1.040
$\Delta\rho_{\text{fin}}$ (max/min), e Å^{-3}	0.11/−0.10	0.18/−0.17	0.13/−1.33

Table 1. Selected crystallographic data and data related to structure solution and refinement of **1**–**3**.

[a] $R1 = \|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (xP)^2 + yP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; [b] $\text{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

the final cycles with anisotropic parameters that gave acceptable values [9]. Hydrogen atoms were added to all C atoms with values of 1.2 U_{iso} of the C atoms. Hydrogen atoms bonded to N and B were taken from the Fourier data and were refined isotropically. All results were checked with the routine CHECKCIF as incorporated in PLATON. They also corroborated the space group *Cc* of **1**. In space group C_2/c no solution was possible. Relevant crystallographic data are summarized in Table 1.

CCDC 721384 (**1**), 721395 (**2**), and 721396 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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[9] Ranges of the C–C distances (min./max. in Å) of the piperidine rings in compound **3**: C1A–C5A 1.523(7)/1.536(8), C1B–C5B 1.525(7)/1.529(7), C6–C10 1.503(6)/1.526(6), C11–C15 1.478(9)/1.528(9), C16–C20 1.494(6)/1.514(6), C21–C25 1.501(6)/1.522(9), C26–C30 1.508(6)/1.522(5), C31–C35 1.497(6)/1.520(6), C36–C40 1.472(7)/1.515(7), C41A–C45A 1.497(7)/1.536(7), C41B–C45B 1.525(7)/1.549(7), C46–C50 1.485(6)/1.509(7), C51–C55 1.506(6)/1.519(6), C56–C60 1.493(5)/1.525(6), C61–C65 1.592(6)/1.517(6), C66–C70 1.484(6)/1.526(6), C71–C75 1.499(5)/1.512(6), C76A–C80A 1.540(8)/1.572(8), C76B–C80B 1.500(7)/1.593(7).