The Structure of Some Amine Solvates of Magnesium Bis(tetrahydroborate) and DFT Calculations on Solvates of Lithium Tetrahydroborate[‡]

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Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday

Keywords: Amine ligands / Borates / Density functional calculations / Lithium / Magnesium

Eight solvates of magnesium bis(tetrahydroborate) have been prepared and characterised by NMR and IR spectroscopy, and five of them also by X-ray crystallography. Compounds $Mg(BH_4)_2{\cdot}3NH_2tBu$ and $Mg(BH_4)_2{\cdot}3pip$ each have a distorted trigonal-bipyramidal structure (with the BH_4 group viewed as a simple ligand) while the putative $Mg(BH_4)_2{\cdot}6py$ proved to be $[Mg(BH_4)_2{\cdot}4py]$ with a pseudooctahedral structure, two py molecules being present as solvent of crystallization. Similarly, $Mg(BH_4)_2{\cdot}8DMSO$ contains the cation $[Mg(DMSO)_6]^{2+}$ in the crystal, and $Mg(BH_4)_2{\cdot}6NH_2Bzl$ has an ionic lattice made up of $Mg(NH_2Bzl)_6{}^{2+}$ and $BH_4{}^-$ ions. The BH_4 groups in the molecular compounds are bonded to the Mg centre through double hydrogen bonds. In order to study the bonding in alkali and alkali earth metal tetrahydroborates, DFT calculations were performed for $LiBH_4$ and its ammonia and dimethyl ether solvates. The minimum-energy structure for a $LiBH_4$ molecule has C_{3v} symmetry; this is not changed when one ammonia molecule is added and is also the result for $LiBH_4{\cdot}3NH_3$. Addition of the first NH_3 or Me_2O molecule contributes more to the stabilisation than a second or a third molecule.

Introduction

The BH_4 anion is a versatile ligand. In mononuclear complexes, one, two or three of its hydrogen atoms may bond to the metal centre. In di-, tri-, and tetranuclear complexes, and also in polymeric compounds, two, three, or even all four hydrogen atoms of the BH_4 ion may be involved in coordination to the metal centres.[1,2] While the structures of the diethyl ether and amine solvates of the alkali metal tetrahydroborates, particularly those of lithium, are fairly well known, there is little structural information on solvates of magnesium bis(tetrahydroborate). So far, only two compounds − $Mg(BH_4)_2{\cdot}3thf$[3,4] and $Mg(BH_4)_2{\cdot}diglyme$ − have been structurally investigated.[5] Both are mononuclear, with $Mg(\mu\text{-}H_2BH_2)_2$ units to which the diethyl ether ligands are coordinated. Although many other solvates of magnesium bis(tetrahydroborate) have been reported,[6−10] no structural information as to the bonding of the BH_4 group is known. In pursuit of our interest in studying the structures of tetrahydroborates of main group metals systematically we have prepared a number of new solvates of $Mg(BH_4)_2$ and determined their crystal structures. Moreover, we also performed DFT calculations on mononuclear $LiBH_4{\cdot}nOMe_2$ and $LiBH_4{\cdot}nNH_3$ in the expectation that they might offer insights into the hydrogen bonding of the BH_4 group and the stability of the solvates.

Preparation and Spectra

Magnesium bis(tetrahydroborate) is regarded as a salt-like compound, due to its comparatively high melting point (180 °C)[11] and very low solubility in non-polar solvents. It was first prepared by Wiberg and Bauer,[12] from Et_2Mg and diborane in diethyl ether solution, while it was later shown by Ashby and Becker that dimeric $EtMgBH_4{\cdot}OEt_2$ is a better starting material.[13] It reacts with diborane in diethyl ether solution to give a solid 2:3 diethyl ether adduct of magnesium tetrahydroborate. Under similar conditions we obtained $Mg(BH_4)_2{\cdot}2OEt_2$ as a viscous oil, which reacts rapidly with moisture [see Equation (1)].

$$EtMg(BH_4) + B_2H_6 \rightarrow Mg(BH_4)_2 + \text{“}EtBH_2\text{''} \quad (1)$$

It is clear that the formation of $Mg(BH_4)_2$ as in Equation (1) requires several steps. ^{11}B NMR spectroscopy gives an insight into the course of the reaction. Figure 1 shows spectra taken at different ratios of $EtMgBH_4/B_2H_6$ in diethyl ether solution. Trace 1 shows the (undecoupled) ^{11}B quintuplet signal of the starting material at $\delta = -43.1$ ppm.

[‡] Metal Tetrahydroborates and Tetrahydroborato Metallates, 28. Part 27: Ref.[1]

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Trace 2 shows in addition a quadruplet and a triplet at δ = −27 and −18 ppm; these are typical for $EtBH_3^-$ and $Et_2BH_2^-$. More diborane (trace 3) gives rise to the formation of more $Et_2BH_2^-$ besides BEt_3 (signal at δ = 86 ppm). Trace 5 reveals that the addition of even more diborane transforms the ethylhydridoborates completely into BH_4^- and ethyldiboranes. Moreover, BEt_3 reacts with diborane to give the ethyldiboranes and the former compound vanishes completely, as shown in trace 6. The 1:1 signal ratio of the broad signal at δ = 42.9 ppm and the triplet of triplets at δ = 4.8 ppm are indicative of the preferred formation of asymmetrically substituted diethyldiborane $Et_2BH_2BH_2$. After removal of all volatiles, only the quintuplet signal of magnesium tetrahydroborate could be noted. The most striking feature of this process is that the anion Et_3BH^- is not observed. We assume that this species reacts very rapidly with "BH_3" to give BEt_3 and BH_4^-. In a similar reaction, Et_2BH is formed by hydride abstraction from $Et_2BH_2^-$ by diborane. Et_2BH then picks up BH_3 to give asymmetrical diethyldiborane. The characterising NMR spectroscopic data are listed in the legend of Figure 1.

It is known from previous work[6−10] that $Mg(BH_4)_2$ readily forms solvates with diethyl ethers and amines. Adducts with ammonia[8,9] and with methylamines[10] are readily available, as is the complex with isopropylamine,[10] but all these adducts deteriorate quickly at ambient temperature. We were, however, able to obtain the last of these compounds as single crystals, but these became rapidly turbid during their isolation at low temperature (ca. −30 °C). In contrast, $Mg(BH_4)_2{\cdot}3H_2NCMe_3$ (**1**) was isolable and stable at −30 °C. All the new compounds, as well as a previously described pyridine adduct,[10] were obtained either by dissolving $Mg(BH_4)_2$ in the amine as solvent or by replacement of THF from $Mg(BH_4)_2{\cdot}3thf$ with a new ligand L′, and crystallisation of the complexes by addition of cyclohexane to the resulting solutions. Reactions proceeded as shown in Equation (2). The compounds listed in Table 1 were obtained. The yields were not optimised, only the material that crystallised or precipitated being isolated.

$$Mg(BH_4)_2{\cdot}n\mathrm{L} + n\,\mathrm{L}' \rightarrow Mg(BH_4)_2{\cdot}n\mathrm{L}' + n\,\mathrm{L} \qquad (2)$$

^{11}B NMR spectra were recorded either in the corresponding amine as solvent or in DMSO. The shielding of the boron nuclei and the coupling constants observed are practically independent of the coordinated ligand (diethyl ethers, amines). The small but significant low-field shift of the ^{11}B NMR signal relative to $NaBH_4$ [$\delta^{11}B = -41$; $^1J(BH) = 82$ Hz] suggests that there is a weak interaction between the tetrahydroborate anion and the Mg cation, but on the other hand, the fairly similar shielding also suggests that $Mg(BH_4)_2$ is present in amine solution as a salt $[Mg(amine)_n](BH_4)_2$, and hence that the solution state is different to the structure in the solid state except in the case of compound **4**. As with most tetrahydroborates, neither the ^{11}B chemical shift nor the coupling constant give a reliable in-

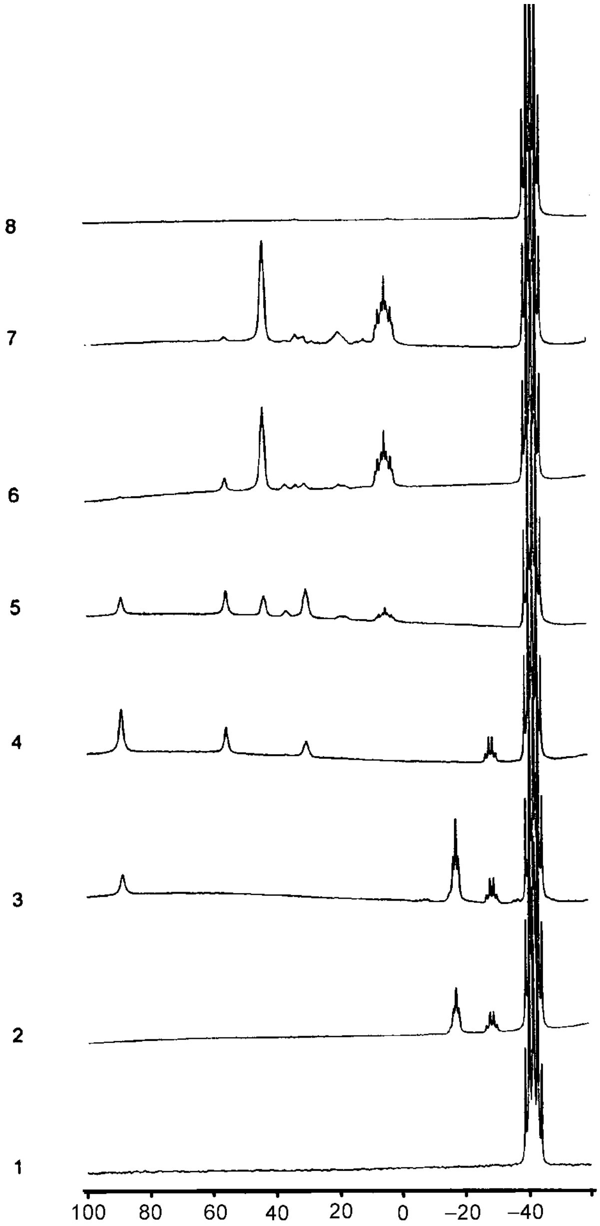


Figure 1. ^{11}B NMR spectra of a solution of $EtMgBH_4$ to which diborane dissolved in diethyl ether was added incrementally; assignment of chemical shifts (in $\delta^{11}B$) are as follows: BH_4^- −43.1, H_3BEt^- −30.3, $H_2BEt_2^-$ −18.1, $H_2\mathit{B}H_2BEt_2$ 4.8, H_2BEt 29.8, $H_2BH_2\mathit{B}Et_2$ 42.9, $HBEt_2$ 54.9, BEt_3 87.3

Table 1. $\delta^{11}B$ [ppm] and $^1J(BH)$ [Hz] values of compounds **1**−**8**

		$\delta^{11}B$	$^1J(BH)$
$Mg(BH_4)_2{\cdot}3H_2NtBu$	**1**	−38.5	82
$Mg(BH_4)_2{\cdot}3HNC_5H_{10}$	**2**	−40.3	82
$Mg(BH_4)_2{\cdot}6py$	**3**	−37.6	82
$Mg(BH_4)_2{\cdot}6H_2NCH_2Ph$	**4**	−37.8	81
$Mg(BH_4)_2{\cdot}2(18\text{-crown-}5)$	**5**	−34.9	81
$Mg(BH_4)_2{\cdot}8DMSO$	**6**	−33.8	79
$Mg(BH_4)_2{\cdot}2deta$	**7**	35.8	82
$Mg(BH_4)_2{\cdot}pmdta$	**8**	−34.5	82

Table 2. Typical IR bands [cm^{-1}]in the B−H stretching region (for ^{11}B isotope) of the tetrahydroborates **1**−**8** and $Mg(BH_4)_2 \cdot 2OEt_2$ (**9**)

1	2369 st	2325 st			2228 st	
4		2327 st	2216 st	2252 st		2182 m
5			2283.4 st		2219.3 st	2149.3 m
6			2282.8 st		2214.1 st	2146.9 st
7			2299.8 st		2234.2 st	2159.0 st
8	2368.8 st	2322.2 st	2275.8 st	2240.9 st	2197.1 st	
9	2391.7 st	2350.8sh	2234.5sh	2185.2st		
$NaBH_4$ [11]	2393 st		2291 st		2229 st	

dication as to the bonding of the BH_4 group to Mg^{2+}. The quintuplet structure of the signal shows four chemically equivalent hydrogen atoms: this may be due to a free anion or to rapid exchange between bridging and terminal hydrogen atoms.[14]

Thanks to its higher time resolution, IR spectroscopy may be more informative as far as the interaction of the cation with the BH_4 anion is concerned. Depending on the type of hydrogen bond the local symmetry of the BH_4 anion changes from C_{3v} to C_{2v} and then to C_{3v} for the single bridge $Mg(H-BH_3)$ to the double bridge $Mg(H_2BH_2)$ and then to the triple bridge $Mg(H_3BH)$. The expected spectra are different for the three types of bonding. For double hydride bridges, four active IR bands, due to two $\nu_{as}BH_2$ vibrations and two $\nu_{sym}BH_2$ vibrations, would be expected, while for C_{3v} symmetry three bands, due to ν_{as} and ν_{sym} for the H_3B group and one stretching frequency for the single B−H bond, should be observable.

The presence of four bands in the IR spectrum of $Mg(BH_4)_2 \cdot 2OEt_2$ thus points to double hydride bridges, and this suggests hexacoordination at the Mg centre (two oxygen and four hydrogen atoms, see Table 2).

In contrast, the crown diethyl ether complex exhibits only three bands, which are found in the same region as for $NaBH_4$,[15] and this is indicative of an ionic structure. The same feature is found for the DMSO compound **6**, but this is not compatible with its $\delta^{11}B$ value (−33.8). The structure in DMSO solution may therefore be different from that in the solid state. One can imagine an equilibrium in solution of a type as shown in Equation (3).

$$Mg(DMSO)_6^{2+} + 2\,BH_4^- \rightleftarrows Mg(DMSO)_5BH_4^+ + BH_4^- + DMSO \quad (3)$$

The diethylenetriamine complex **7** shows an IR spectrum typical of free BH_4 anions in the BH stretching range. This compound should therefore have the constitution $[Mg(deta)_2](BH_4)_2$, with hexacoordinated Mg ions. In contrast, complex **8** − which contains only one molecule of the amine − has five BH bands in the stretching region. This indicates that it most probably has the structure $[Mg(pmdta)H_2BH_2]BH_4$.

Crystal Structures

In order to investigate the type of hydride bridging between the BH_4 anion and the Mg ion in the solid state, single crystals of **1**−**4** and also of **6** were studied by X-ray crystallography. The $tBuNH_2$ solvate **1** crystallises in the monoclinic space group $P2_1/n$ with $Z = 8$ (i.e., there are two independent molecules in the asymmetric unit). The molecular parameters of the two molecules are fairly similar, and so only one of them is depicted in Figure 2. Both BH_4 groups in the molecule are bonded to the magnesium ion through two hydrogen atoms. A distorted trigonal-bipyramidal arrangement of two boron and three nitrogen atoms around the magnesium centre is observed, with two nitrogen atoms in the apical positions. The apical Mg−N distances are longer [2.243(2), 2.277(2) Å] than the equatorial Mg−N bond [2.212(2) Å]. The atoms Mg1, B1, B2, and N2 lie almost in a perfect plane. Interestingly, the B−Mg−B angle is quite open, at 137.87(8)°. The Mg···B distances in **1** are on average 0.097 Å longer than in $Mg(BH_4)_2 \cdot 3thf$.[3,4] Although all hydrogen positions around the boron atoms were found in the difference Fourier map and refined well, the B−H distances nevertheless have to be regarded as approximate distances.

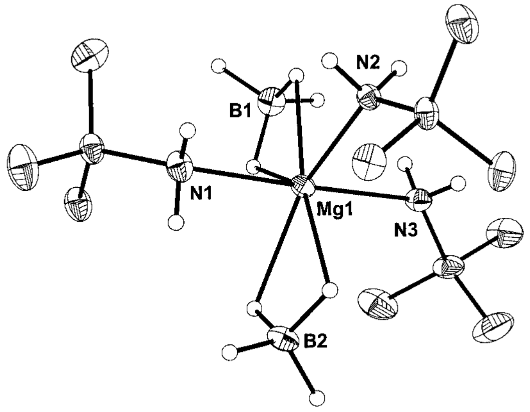


Figure 2. The molecular structure of compound **1**; thermal ellipsoids are represented on a 25% probability scale; selected atom distances (in Å) and bond angles (in °): Mg1−N1 2.243(2), Mg1−N2 2.212(2), Mg1−N3 2.227(2), Mg···B1 2.549(2), Mg1···B2 2.521(2), Mg−H_{br} 2.08 (aver.), B−H_{br} 1.15(1) (aver.), B−H_{term} 1.12(1) (aver.); B1−Mg1−B2 137.8(8), N1−Mg1−N2 89.48(6), N1−Mg1−N3 177.55(7), N2−Mg−N3 90.44(7)

In principle, the same molecular structure as for **1** was found for **2** (see Figure 3). However, this molecule crystallises in the triclinic system with the centrosymmetric space group $P\bar{1}$, $Z = 2$. In contrast to **1**, one of the two apical N atoms has a short Mg−N bond [2.233(4) Å] while the second [2.249(4) Å] is longer, practically as long the equatorial Mg−N distance [2.244(4) Å]. Moreover, the two Mg···B distances are quite different, although their average value corresponds to the Mg···B distance found for **1**.

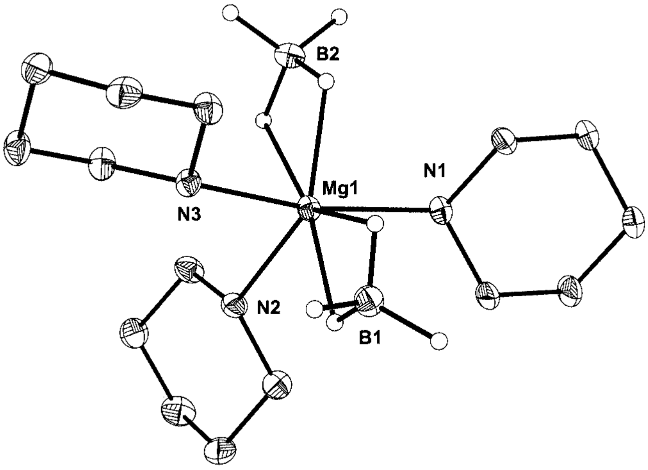


Figure 3. The molecular structure of compound **2**; thermal ellipsoids are represented on a 25% probability scale; selected atom distances (in Å) and bond angles (in °): Mg1−N1 2.233(4), Mg1−N2 2.244(4), Mg1−N3 2.249(4), Mg1···B1 2.536(6), Mg1···B2 2.520(6), Mg−H 1.99(5) (aver.), $\mathrm{B-H_{br}}$ 1.12(5) (aver.), $\mathrm{B-H_{term}}$ 1.15(5) (aver.); B1−Mg1−B2 143.6(2), N1−Mg1−N2 102.2(2), N1−Mg1−M3 165.0(2), N2−Mg1−N3 92.7(2)

The composition of the pyridine complex of $\mathrm{Mg(BH_4)_2}$ suggested an ionic structure $\mathrm{[Mg(py)_6](BH_4)_2}$. This is not the case, however, as shown by the X-ray structure analysis of the orthorhombic crystals, space group *Ccca* (see Figure 4). The asymmetric unit contains molecular $\mathrm{Mg(BH_4)_2{\cdot}4py}$, and in addition there are two pyridine molecules. The $\mathrm{Mg(BH_4)_2{\cdot}4py}$ molecule possesses D_2 point group symmetry. All its pyridine molecules are arranged in a plane around the Mg centre, while the boron atoms stand perpendicularly on the $\mathrm{MgN_4}$ plane. Thus, the geometry for the $\mathrm{MgB_2N_4}$ unit is a distorted octahedron with the Mg atom in its centre. In agreement with the higher coordination number, the Mg···B distances are longer than those in **1** and **2**, but these lengths are considerably greater than would be expected. As a consequence, the Mg−H bond lengths are also long, and one should note, although with caution, that the bridging hydrogen B−H bond lengths are shorter than those of the terminal B−H bonds. On the other hand, the Mg−N bond lengths [varying from 2.197(2) to 2.224(3) Å] are longer than in **1** or **2**. One might argue that the difference in Mg−N bond length could be smaller because of the sp^2-type N atoms of the pyridine molecules.

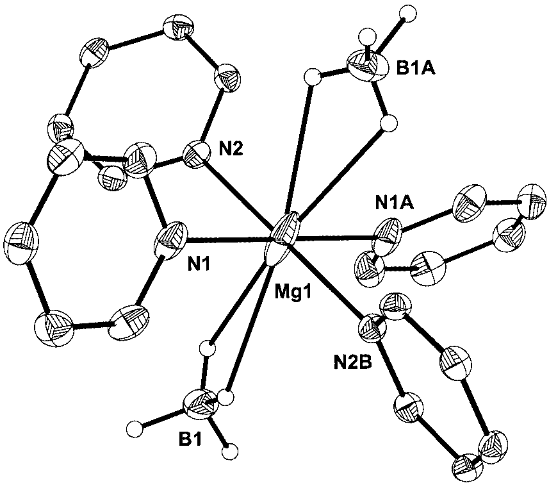


Figure 4. The molecular structure of compound **3**; thermal ellipsoids are represented on a 25% probability scale; selected atom distances (in Å) and bond angles (in °): Mg1−N1 2.224(3), Mg1−N2 2.197(2), Mg1···B1 2.988(4), $\mathrm{Mg1-H_{br}}$ 2.40(4) (aver.), $\mathrm{B-H_{br}}$ 0.98(5), $\mathrm{B-H_{term}}$ 1.13(3); B1−Mg1−B1A 180, B1−Mg1−N1 90, N1−Mg1−N1A 180

In contrast to the molecular compounds, the benzylamine adduct **4** proved to be ionic. The crystals are monoclinic, space group $P2_1/c$, $Z = 4$. Figure 5 shows the cation, together with a $\mathrm{BH_4}$ anion and two further boron atoms. The sites of these two boron atoms are occupied with SOFs of 0.5 on inversion centres. Although the highest residual electron densities are found around these boron atoms, assignment to boron-bonded hydrogen atoms was not possible. It should be noted that a set of tetrahedrally oriented H atoms would, by symmetry, be transformed into eight H positions about these boron atoms, and SOFs of 0.5 would be expected for these hydrogen atoms. It follows that it would be unlikely that these could be well located, because of the expected very low electron density for these hydrogen atoms.

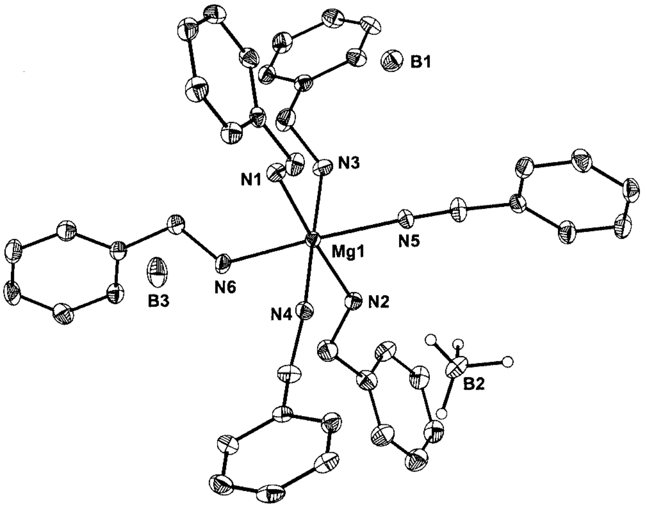


Figure 5. The molecular structure of compound **4**; thermal ellipsoids are represented on a 25% probability scale; selected atom distances (in Å) and bond angles (in °): Mg1−N1 2.252(2), Mg1−N2 2.247(2), Mg1−N3 2.263(2), Mg1−N4 2.258(2), Mg1−N5 2.258(2), Mg1−N6 2.233(2); N1−Mg1−N2 176.50(9), N1−Mg1−N3 89.92(8), N1−Mg1−N4 87.88(8), N1−Mg1−N5 89.62(8), N1−Mg1−N6 91.23(9), N3−Mg1−N4 176.89(6), N5−Mg1−N6 176.95(5)

The Mg ion occupies a slightly distorted octahedral environment. One of the six Mg−N bonds is significantly shorter [2.233(2) Å] than the other five [2.247−2.263(2) Å]. The N−Mg−N bond angles of adjacent N atoms range from 87.88(8) to 91.23(9)°, while those of opposite N atoms are practically identical [176.89(9) to 176.95(9)°].

Figure 6 shows the structure of compound **6**. The asymmetric unit of the cell is $[Mg(DMSO)_6]_{1/2}\cdot(BH_4)\cdot DMSO$. A symmetry operation through an inversion centre generates the cation $Mg(DMSO)_6^{2+}$ and an additional BH_4, besides a DMSO molecule. The Mg−O distances range from 2.056 through 2.072 to 2.093(2) Å, and the O−Mg1−O bond angles are consequently 180° for opposite oxygen atoms and very close to 90° for adjacent oxygen atoms. The S−O bond lengths of the coordinated DMSO molecules are slightly longer [1.516 to 1.521(2) Å] than those in the free DMSO molecule [1.501(3) Å], while the S−C bonds are slightly shorter for coordinated DMSO [aver. 1.769(5) Å] than for non-coordinated DMSO (1.779 Å). On the other hand the O−S−C bond angles in the coordinated DMSO molecules are slightly smaller than those in free DMSO.

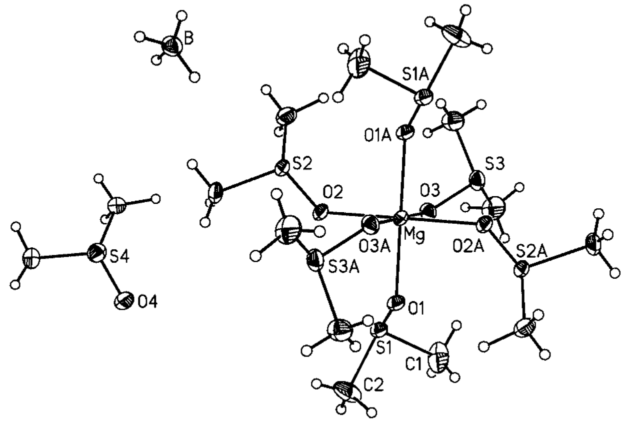
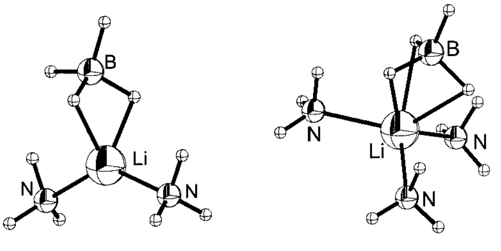


Figure 6. The molecular structure of compound **6**; thermal ellipsoids are represented on a 25% probability scale; selected atom distances (in Å) and bond angles (in °): Mg1−O1 2.056(2), Mg1−O2 2.093(2), Mg1−O3 2.072(2), B1−H1 1.10(4), B1−H2 0.75(4), B1−H3 1.02(4), B1−H4 1.15(4), S1−O1 1.520(2), S1−C1 1.769(5), S1−C2 1.769(5), S2−O2 1.521(2), S3−O3 1.516(2), S4−O4 1.501(3), S4−C7 1.781(5), S4−C8 1.777(5); O1−Mg1−O1A 180; O1−Mg1−O2 89.86(9), O1−Mg1−O2A 90.14(9), O1−Mg1−O3 90−20(9), O1−Mg1−O3A 89.80(9), H−B−H 92−122(3), S1−O1−Mg1 124.8(1), O1−S1−C1 104.9(2), O1−S1−C2 103.7(2), C1−S1−C2 97.4(2), S2−O2−Mg1 118.6(1), O2−S2−C3 105.2(2), O2−S2−C4 105.1(2), C3−S2−C4 98.4(3), S3−O3−Mg1 122.7(1), O3−S3−C5 105.9(2), O3−S3−C6 104.1(2), O4−S4−C7 107.1(2), O4−S4−C8 106.2(2), C7−S4−C8 96.7(2)

DFT Calculations

As far as magnesium tetrahydroborates are concerned, the structures determined so far show that only $\mu_2{}^1$ bonding (double hydride bridge to a single central atom) of the tetrahydroborate ion is present irrespective of the solvate ligand. In contrast, $LiBH_4$ forms a large variety of solvates with different types of bonded BH_4 groups ranging from molecular units with $\mu_2{}^1$-$\mu_3{}^1$-bonded BH_4 anions to dimers with two $2\mu_1{}^1$-$\mu_1{}^2$ BH_4 groups (two single and one H atom bridging two Li ions) to polymeric structures in which all H atoms of the BH_4 anion are involved.[1,16] Such a situation is also observed in the linear polymeric structure of $Ba(BH_4)\cdot 2thf$.[17] It was therefore of interest to obtain some insight into what should be expected when the $LiBH_4$ molecule is solvated, as these results may also be important for other alkali metal and alkaline earth metal tetrahydroborate compounds. For this reason we conducted DFT calculations on free $LiBH_4$ molecules and some of their ammonia and dimethyl ether solvates. These calculations were performed by use of the Gaussian 98 program package.[18] All calculations were conducted at the B3LYP level of theory[18,19] with the triple ξ basis set 6-311++G(d,p).[20] A frequency analysis after geometry optimisation showed no imaginary frequencies, and so the geometry represents a minimum on the energy hypersurface.

As the BH_4 anion approaches the Li cation, one would expect that the bond of the bridging hydrogen atoms should become longer than the terminal B−H bonds. This difference should increase as the BH_4 group becomes more polarized by the Li cation. Since it is difficult to determine the B−H distances reliably by X-ray diffractometry it is advisable to inspect the stretching frequencies of the B−H bonds (Scheme 1). Tables 3, 4, and 5 summarise the point group symmetries, the calculated wavenumbers of the B−H stretching vibrations and the calculated B−H bond lengths. Calculations with H_2O as a ligand could not be performed successfully as there is always a hydride−proton interaction giving rise to a very strong distortion. We therefore used dimethyl ether as the model for Li−O interactions. It should be noted that a distorted μ_2 coordination was found for $LiBH_4\cdot 2NH_3$; it is not included in the data of Table 5.



Scheme 1. Calculated geometries for $LiBH_4$ |1582NH_3 and $LiBH_4$ |1583NH_3 (see Table 3)

First, it follows that, on using a larger basis set for the $LiBH_4$ molecules of point group symmetry C_{3v}, significant differences result for $\nu_{sym}BH_{br}$ but particularly for νBH_{term}. Addition of NH_3 to $LiBH_4$ strengthens the bridging B−H bonds and weakens the terminal B−H bond, while addition of three ammonia molecules produces a remarkable weakening of the BH_{term} bond and a strengthening of the bridging B−H bonds. The same trend holds for the dimethyl ether adducts.

On the other hand, the calculated B−H distances, and in particular the Li···B atom distances, increase with increasing coordination number at the cation. Table 3 shows a comparison of calculated and observed Li···B, Li···N, and Li−H distances. The calculated and observed data (but not the trend) are compatible.

Moreover, the trend in bonding should be reflected by the calculated electronic energies (Table 4). The data given are corrected by unscaled zero point energies and are relative to $LiBH_4$ with C_{3v} point group symmetry and triple hydride bridging. Data for the solvated $LiBH_4$ molecule are

Table 3. Relative changes in energy with variation of coordination of the tetrahydridoborate anion and the solvation of the Li cation

Compound	Point group	Relative energy[a] [kJ/mol]	Ref.[b] [kJ/mol]	Ref.[c] [kJ/mol]	Ref.[d] [kJ/mol]
Li(μ_1-HBH$_3$)	C_{3v}	109[e]	125	113	
Li(μ_2-H$_2$BH$_2$)[b]	C_{2v}	19[f]	24	23	15
Li(μ_3-H$_3$BH)	C_{3v}	0	0	0	0
(LiBH$_4$)$_2$	C_1	−68			−79
LiBH$_4$·NH$_3$	C_3	−84			
LiBH$_4$·2NH$_3$	C_1	−132			
LiBH$_4$·3NH$_3$	C_1	−165			
(LiBH$_4$·NH$_3$)$_2$	C_1	−172			
LiBH$_4$·OMe$_2$	C_1	−87			
LiBH$_4$·2OMe$_2$	C_1	−141			
LiBH$_4$·3OMe$_2$	C_1	−175			

[a] Method B3LYP/6-311++G(d,p). [b] Method HF/6-31G(d,p); A. A. Gorbik, O. P. Carkin, *Russ. J. Inorg. Chem.* **1985**, *30*, 1711−1714. [c] Method HF/6-31G(d)//HF/STO-3G; J. D. Dill, P. v. R. Schleyer, J. S. Binkley, J. A. Pople, *J. Am. Chem. Soc.* **1977**, *99*, 6159−6173. [d] Method HF/6-31G; geometries partially fixed; D. R. Armstrong, W. Clegg, D. S. Jones, W. N. Lipscomb, *Chem. Phys. Lett.* **1987**, 630−632. [e] Forced by fixed geometry; two imaginary frequencies. [f] Forced by fixed geometry; one imaginary frequency.

Table 4. Comparison between calculated [B3LYP/6-311++G(d,p)] and experimentally determined (X-ray) bond lengths (values in Å are in part averaged)

	Calculation	X-ray structure	Calculation	X-ray structure
	LiBH$_4$·2NH$_3$	LiBH$_4$·2(collidine) (**2**)	LiBH$_4$·3NH$_3$	LiBH$_4$·3(aniline) (**7**)
Li−B	2.172	2.252(6)	2.232	2.135(2)
Li−N	2.056	2.051(3)	2.129	2.279(6)
B−H$_{br}$	1.246	1.17(2)	1.235	1.10(4)
B−H$_{term}$	1.215	1.14(2)	1.205	0.86(5)
Li−H$_{br}$	1.819	1.81(2)	2.129	1.96(4)

Table 5. Effect on coordination and solvation of the tetrahydroborate ion [B3LYP/6-311++G(d,p), if not otherwise stated]

Compound	Point group	Vibration frequencies (in cm^{-1})			Bond lengths (in Å)		
		ν_{asym}(BH$_{br}$)	ν_{sym}(BH$_{br}$)	ν(BH$_{term}$)	B−H$_{br}$	B−H$_{term}$	M−B
BH$_4^-$	T_d	2226 (T)			1.238		–
LiBH$_4$	C_{3v}	2210 (E)	2249	2594	1.244	1.193	1.914
LiBH$_4$ [a]	C_{3v}	2216 (E)	2256	2606	1.243	1.191	1.914
NaBH$_4$	C_{3v}	2206 (E)	2240	2521	1.242	1.201	2.288
KBH$_4$	C_{3v}	2215 (E)	2248	2493	1.241	1.205	2.648
HMgBH$_4$	C_{3v}	2217 (E)	2241	2640	1.246	1.187	2.117
NH$_3$·LiBH$_4$	C_3	2220 (E)	2253	2566	1.243	1.196	1.954
3NH$_3$·LiBH$_4$	C_1	2271/2273	2284	2488	1.235	1.205	2.232
OMe$_2$·LiBH$_4$	C_1	2216/2226	2255	2565	1.243	1.196	1.955
2OMe$_2$·LiBH$_4$	C_1	2231/2247	2311	2526	1.238	1.201	2.044
3OMe$_2$·LiBH$_4$	C_1	2268/2284	2296	2499	1.235	1.204	2.116

[a] Calculated with a larger basis set B3LYP/6-311++G(3df,3pd).

also scaled for Li(H$_3$BH) and free solvent molecules with $E = 0$ kJ/mol.

There is an energy difference of 90 kJ/mol between singly and doubly bridged LiBH$_4$, while the energy difference between the latter and the triply bridged molecule is only 19 kJ/mol. Dimerization of LiBH$_4$ affords a stabilization by 68 kJ/mol, and successive addition of ammonia produces a large stabilization for the addition of the first molecule, and less for each other step as one adds two or three molecules. LiBH$_4$·3NH$_3$ is the most stable monomeric arrangement. Calculations also show that (LiBH$_4$·NH$_3$)$_2$ is 7 kJ/mol more stable than LiBH$_4$·3NH$_3$. A similar trend holds for the dimethyl ether adducts of LiBH$_4$. These adducts are more stable than the solvates with ammonia molecules.

Discussion

At present, only two types of magnesium bis(tetrahydroborates) are known: molecular mononuclear solvates and ionic mononuclear complexes. The structure of solvent-free $Mg(BH_4)_2$ is still unknown, but in view of the effective radii of Br^- and BH_4^-, which are very similar, one might expect that $Mg(BH_4)_2$ should have the same structure as $MgBr_2$. Thus, $MgBr_2$ forms THF solvates such as $MgBr_2{\cdot}3THF$.[21,22] While a multitude of different bonding situations has been found for $LiBH_4$, ranging from solvated mononuclear to polymeric species,[1,16] only one type of bonding has so far been detected for $Mg(BH_4)_2$: $Mg(\mu_2{}^1\text{-}H_2BH_2)$, irrespective of the number of additional ligands associated with Mg^{2+}. For instance, $Mg(BH_4)_2{\cdot}3THF$, **1** and **2** can be regarded as deriving from a trigonal-bipyramidal geometry[3,4] if we involve the boron atoms in bonding and neglect the bridging hydrogen atoms. If we consider only the nearest neighbours to magnesium, then the coordination number is 7 (four H and three N or O atoms). Compound **3** can be viewed as distorted octahedral, the Mg ion coordinated to four N and two B atoms, or as octacoordinated (four H and four N atoms).

The second type is ionic, with the general composition $[MgL_6](BH_4)_2$ (compounds **4**, **6** and most probably also **7**). These compounds are formed if the donor numbers of the solvent molecules are high.[23] The order of increasing donor strength found for $Mg(BH_4)_2$ is: ether < THF < NH_2tBu ≈ pip < py < NH_2Bzl < DMSO. In comparison with complexes of the other alkali earth metals, the order $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+}$ demonstrated by Irvin and Williams[24,25] is compatible with the solvates of these alkali earth metal tetrahydroborates.

It is astonishing that no di- or trinuclear solvates of magnesium bis(tetrahydroborate) are yet known; one might expect that solvates of the type $L_2(BH_4)Mg(BH_4)_2Mg(BH_4)L_2$ should be stable by analogy to $MgBr_2{\cdot}2THF$, which forms a polymer in the solid state with hexacoordinated Mg^{2+}.[22] Thus, there is no reason why solvates of magnesium bis(tetrahydroborate) should not have as rich a structural chemistry as the solvates of $LiBH_4$.

Experimental Section

General: All experiments were performed under anhydrous conditions by use of Schlenk techniques and dinitrogen as a protecting gas. The amines used were distilled before use. $Mg(BH_4)_2$ was prepared from $EtMgBH_4$ [13,26] and diborane in diethyl ether. NMR: Jeol XL400, $BF_3{\cdot}OEt_2$ as external standard. IR: Nicolet 520 FT-IR or Perkin−Elmer 325 (samples in Nujol): X-ray: Siemens P4 diffractometer equipped with an LT2 low-temperature device and a CCD area detector for compounds **1**−**4**. Data for compound **6** were collected with a scintillation counter in the ω/2θ mode. Mo-K_α radiation, graphite monochromator.

Magnesium Bis(tetrahydridoborate) Bis(diethyl ether) (9): A solution of iodine (25.4 g, 100 mmol) in diglyme (50 mL) was slowly added to a stirred solution of $NaBH_4$ (7.5 g, 200 mmol) in diglyme (30 ml). The diborane generated was carried by a stream of N_2 into a solution of $EtMgBH_4$ (25 mmol) in diethyl ether (100 mL). After this solution had been stirred for 2 h, all volatile components were removed in vacuo (1 Torr). The diethyl ether adduct of $Mg(BH_4)_2$ was a solid that liquefied on standing at ambient temperature. The coordinated diethyl ether could be removed (monitoring by weight loss) by keeping the compound in high vacuum (0.001 Torr) for 12 h. Yield of **9**: 4.75 g (93.8%). $\delta^{11}B$ (ether) = −43.0 [^1J(BH) = 82.4 Hz] ppm. δ^1H (C_6D_6) = 0.21 [q, ^1J(HB) = 82 Hz], 0.90 (t, CH_3), 3.61 (q, CH_2) ppm. $\delta^{13}C$ (C_6D_6) = 65.7 (CH_2), 13.7 (CH_3) ppm. $C_8H_{28}B_2MgO_2$ (202.25): calcd. H^- 3.98, B 10.69, Mg 12.02; found H^- 3.71, B 10.55, Mg 12.03.

Magnesium Bis(tetrahydroborate) Tris(*tert*-butylamine) (1): $Mg(BH_4)_2$ (134 mg, 2.78 mmol) was dissolved in *tert*-butylamine (15 mL). Methylcyclohexane (5 mL) was added with stirring. This addition caused the precipitation of a small amount of a solid, which was discarded. The filtrate was kept at 8 °C for a week. Colourless prisms separated and were isolated by filtration. The crystals deteriorated rapidly when a stream of dinitrogen was passed over them. Therefore, some of these crystals were removed from the supernatant liquid and placed in perfluoroether oil for X-ray diffraction. The composition is the result of the structure determined by X-ray crystallography. Yield: 280 mg (37%). M.p. 134−136 °C (dec., sealed capillary). $\delta^{11}B$ = −38.5 [^1J(BH) = 82 Hz] ppm. IR: ṽ = 2422 (sh), 2369 (st), 2325 (st), 228 (st) cm^{-1}.

Magnesium Bis(tetrahydroborate) Tris(piperidine) (2): $Mg(BH_4)_2$ (178 mg, 3.29 mmol) was dissolved in piperidine (10 mL), and cyclohexane (5 mL) was added to the stirred solution. Insoluble material was removed from the turbid solution. The filtrate was stored at 8 °C. Colourless prisms of composition $Mg(BH_4)_2{\cdot}3$pip (as determined by X-ray crystallography) were isolated. Yield: 298 mg (29%). M.p. 50−53 °C (dec.). $\delta^{11}B$ (piperidine) = −40.3 [^1J(BH) = 82 Hz] ppm.

Magnesium Bis(tetrahydroborate) Hexakis(pyridine) (3): $Mg(BH_4)_2$ (94 mg, 1.7 mmol) and 1,3,5-trimethyl-1,3,5-triazine (0.25 mL, 1.78 mmol) were dissolved in pyridine (10 mL). Cyclohexane (2 mL) was added with stirring. A colourless solid precipitated and was removed by filtration. Storage at 8 °C gave crystals of composition $Mg(BH_4){\cdot}6$py. Yield: 130 mg (14%). M.p. 57 − 59 °C (dec.). Attempts to obtain compound **3** from $Mg(BH_2)_4$ and pyridine in the absence of the triazine gave no crystals but only oily products. $\delta^{11}B$ = −37.6 [^1J(BH) = 82 Hz] ppm.

Magnesium Bis(tetrahydroborate) Hexakis(benzylamine) (4): Cyclohexane (5 mL) was added to a solution of $Mg(BH_4)_2$ (196 mg, 3.62 mmol) in benzylamine (25 mL). The solid that formed was removed by filtration and the filtrate was cooled to −35 °C. After 3 weeks, colourless prisms had formed and were isolated. Yield: 1.33 g (53%). M.p. 59−60 °C (dec.). $\delta^{11}B$ (benzylamine) = −37.8 [^1J(BH) = 83 Hz)] ppm. IR: ṽ = 2327 (sh), 2316 (st), 2252 (st), 2182 (st) cm^{-1}. $C_{42}H_{62}B_2MgN_6$ (696.5): calcd. C 72.38, H 8.97, N 12.06; found C 71.10, H 8.55, N 12.00.

Magnesium Bis(tetrahydroborate) Bis(15-crown-5) (5): $Mg(BH_4)_2{\cdot}3THF$[3] (3.78 g, 14.0 mmol) was dissolved in THF (40 mL), and 15-crown-5 (5.6 mL, 28 mmol) was added dropwise to the stirred solution. This resulted in the formation of a precipitate, which was isolated by centrifugation and then dried in vacuo. No single crystal could be obtained. Yield: 6.64 g (96.1%). M.p. 311−313 °C. $C_{20}H_{48}B_2MgO_{10}$ (494.52): calcd. C 48.58, H 9.78, H^- 1.63, B 4.37; found C 48.92, H 9.91, H^- 1.59, B 4.31.

Magnesium Bis(tetrahydroborate) Octakis(dimethyl sulfoxide) (6): tBuSMg$(BH_4){\cdot}OEt_2$[26] (1.24 g, 5.7 mmol) was dissolved in a min-

Table 6. Data relating to crystallography, data collection and structure solution of compounds **1−4** and **6**

	1	**2**	**3**	**4**	**6**
Empirical formula	$C_{12}H_{41}B_2MgN_3$	$C_{15}H_{41}B_2MgN_3$	$C_{30}H_{38}B_2MgN_6$	$C_{42}H_{58}B_2MgN_6$	$C_{16}H_{56}B_2MgO_8S_8$
Formula mass	273.41	309.44	528.59	692.87	679.02
Crystal size [mm]	0.30×0.30×0.30	0.10×0.30×0.30	0.20×0.20×0.30	0.20×0.30×0.30	0.35×0.2×0.15
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic	triclinic
Space group	*P*2(1)/*n*	$P\bar{1}$	*Ccca*	*P*2(1)/*c*	$P\bar{1}$
a [Å]	18.9389(9)	10.758(2)	11.604(2)	14.421(1)	9.853(3)
b [Å]	12.4814(6)	10.983(2)	15.114(2)	20.223(2)	10.073(3)
c [Å]	18.9867(9)	11.184(2)	17.190(2)	14.528(1)	11.430(3)
α [°]	90	86.201(3)	90	9	64.66(1)
β [°]	111.4190(1)	61.602(4)	90	90.1720(1)	68.05(2)
γ [°]	90	61.788(3)	90	90	84.72(2)
V [Å^3]	4178.2(3)	1002.7(3)	3014.7(7)	4237.0(6)	948.7(5)
Z	4	2	4	4	1
ρ(calcd.) [Mg/m^3]	0.869	1.025	1.165	1.086	1.189
μ [mm^{-1}]	0.077	0.087	0.088	0.077	0.518
F(000)	1248	348	1128	1496	366
Index range	$-24 \le h \le 24$ $-16 \le k \le 16$ $-24 \le l \le 24$	$-14 \le h \le 13$ $-14 \le k \le 14$ $-14 \le l \le 14$	$-13 \le h \le 13$ $-16 \le k \le 16$ $-20 \le l \le 20$	$-18 \le h \le 18$ $-26 \le k \le 26$ $-14 \le l \le 19$	$-1 \le h \le 10$ $-10 \le k \le 10$ $-12 \le l \le 12$
2θ [°]	58.00	58.02	49.38	58.96	59.98
T [K]	183(2)	193(2)	183(2)	193(2)	173(2)
Refl. collected	23965	5915	7201	24949	3992
Refl. unique	8161	3109	1233	8120	3443
Refl. observed (4σ)	4143	2578	948	4870	3100
R (int.)	0.0442	0.0241	0.0285	0.0489	0.0255
No. variables	422	230	95	479	244
Weighting scheme[a] *x*/*y*	0.0538/0.000	0.0991/3.071	0.0611/3.4174	0.0945/1.6511	0.0652/0.4550
GOOF	0.888	1.152	1.077	1.037	1.043
Final *R* (4σ)	0.0434	0.0938	0.0464	0.0634	0.0482
Final *wR*2	0.0929	0.2626	0.1305	0.1694	0.0772
Largest residual peak [e/Å^3]	0.216	0.520	0.368	0.625	0.419

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

imum amount of DMSO. Ether was allowed to diffuse into this solution over 3 d. Colourless, clear crystals formed during this period and proved to be **6**. The compound hydrolyses only very slowly in air. Yield: 0.88 g (22%). M.p. 118−121 °C. δ^1H ([D$_6$]DMSO) = −0.33 [q, ^1J(HB) = 79.1 Hz] ppm. $C_{16}H_{56}B_2MgO_8S_8$ (679.07): calcd. C 28.30, H 8.31, H$^-$ 1.18, B 3.18, Mg 3.58; found C 27.80, H 8.35, H$^-$ 1.22, B 3.24, Mg 3.48.

Magnesium Bis(tetrahydroborate) Bis(diethylenetriamine) (7): Diethylenetriamine (5 mL, 49 mmol) was added dropwise to a stirred THF solution (50 mL) of $Mg(BH_4)_2{\cdot}3THF$ (3.38 g, 12.5 mmol). This resulted in the immediate precipitation of a colourless solid. After the mixture had been stirred for an additional hour, the solid was isolated by centrifugation. The product did not dissolve in diethyl ether but did so readily in DMSO. Ether was allowed to diffuse into this solution over several days. Clear crystals of **7** separated. These can be kept in air for several minutes without noticeable hydrolysis. Yield: 3.12 g (96.3% before crystallisation). M.p. 298−301 °C. δ^1H ([D$_6$]DMSO) = −0.33 [q, ^1J(HB) = 81.5 Hz], [sept, ^1J(H^{10}B) = 27.3], 3.40 (m, 4 H), 3.31 (m, 4 H) ppm. δ^{13}C (DMSO) = 52.3, 41.4 ppm. $C_8H_{34}B_2MgN_6$ (260.32): calcd. C 36.91, H 13.16, H$^-$ 3.09, B 8.38, Mg 9.34, N 32.27; found C 37.97, H 12.73, H$^-$ 2.98, B 8.31, Mg 9.29, N 31.99.

Magnesium Bis(tetrahydroborate) *N,N,N′,N′,N′′*-Pentamethyldiethylenetriamine (8): Pentamethyldiethylenetriamine (5 ml, 38 mmol) was added with stirring to a solution of $Mg(BH_4)_2{\cdot}3THF$ (2.87 g, 10.6 mmol) in THF (50 mL). The solution was kept at −18 °C for 24 h. Over this time clear needles separated; these hydrolysed rapidly on contact with air or water. Yield: 1.52 g (63.1%). δ^1H ([D$_6$]DMSO) = −0.32 [q, ^1J(H^{11}B) = 81.9 Hz, sept, ^1J(H^{10}B) = 28.0 Hz], 2.51 (s, 3 H, MeN), 2.62 (t, 4 H, Me$_2$NC*H*$_2$), 2.71 (t, 4 H, MeNC*H*$_2$), 3.73 (s, 12 H, NMe$_2$) ppm. δ^{13}C = 42.9 (MeN), 45.8 (NMe$_2$), 56.0 (Me$_2$N*C*), 57.9 (MeN*C*) ppm. $C_9H_{31}B_2MgN_3$ (227.29): calcd. C 47.56, H 13.75, H$^-$ 3.54, B 9.51, N 18.49, Mg 10.69; found C 46.39, H 12.96, H$^-$ 3.47, B 9.43, N 16.57, Mg 10.58.

X-ray Structure Determinations: Crystals were covered with perfluoropolyether oil and selected under dinitrogen gas. They were placed on a glass fibre, mounted on a goniometer head and cooled to −80 °C by means of a Siemens LT2 low-temperature device. After cell determination, the data were collected in the hemisphere mode (implemented in the program SMART[27]) on 1284 frames. Data reduction was performed with the program SAINT,[28] and the structure was solved and refined with the SHELX programmes.[29] Parameters for non-hydrogen atoms were anisotropically refined, and the hydrogen atoms bonded to the boron atoms were placed in the found positions while the CH hydrogen atoms were placed in calculated positions. Isotropic thermal parameters for the boron-bonded hydrogen atoms were freely refined but fixed in the final cycles of the refinement. A summary of relevant data is given in Table 6. Additional crystallographic data for the structures were deposited with the Cambridge Crystallographic Data Centre as supplementary publications numbers CCDC-186646 (**1**), -186647 (**2**), -186648 (**3**), -186649 (**4**) and -186650 (**6**). These can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.as.uk].

Acknowledgments

We thank the Fonds der Chemischen Industrie and particularly Chemetall GmbH for support of this work. We also acknowledge the help by Mr. Peter Mayer for many measurements, and Mrs. E. Kiesewetter for recording IR spectra.

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[1] J. Knizek, H. Nöth, *J. Organomet. Chem.* **2000**, *614/615*, 168−187.

[2] H. H. Giese, J. Knizek, H. Nöth, M. Warchhold, *Eur. J. Inorg. Chem.* **2001**, 1195−1206.

[3] H. Nöth, *Z. Naturforsch., Teil B* **1982**, *37*, 1499−1503.

[4] E. B. Lobkovski, L. V. Titov, S. B. Psirka, M. Yu, *Antipin Zh. Struct. Khim.* **1982**, *23*, 172−174.

[5] V. N. Konoplev, T. A. Silina, *Koord. Khim.* **1988**, *33*, 2363−2366; E. B. Lobkovski, L. V. Titov, M. D. Lecicheva, A. N. Chelkhov, *Zh. Strukt. Khim.* **1990**, *31*, 147−153.

[6] V. N. Konoplev, T. A. Silina, A. S. Sizarea, *Koord. Khim.* **1988**, *18*, 451−455.

[7] V. N. Konoplev, V. I. Mikheeva, *Zh. Neorg. Khim.* **1965**, *10*, 2363−2364.

[8] V. N. Konoplev, T. A. Silina, *Zh. Neorg. Khim.* **1985**, *5*, 1125−1127.

[9] R. W. Parry, D. R. Shultz, *J. Am. Chem. Soc.* **1958**, *80*, 4−8.

[10] S. Heřmanek, J. Plešek, *Collect. Czech. Chem. Commun.* **1966**, *31*, 3845−3849.

[11] E. Wiberg, R. Bauer, *Z. Naturforsch., Teil B* **1952**, *5*, 58−59.

[12] E. Wiberg, R. Bauer, *Z. Naturforsch., Teil B* **1950**, *3*, 397.

[13] E. C. Ashby, W. Becker, *Inorg. Chem.* **1975**, *4*, 1816−1818.

[14] For a survey see: H. Nöth, B. Wrackmeyer, "Nuclear Magnetic Resonance Spectroscopy of Boron Compounds", in: *NMR Basic Principle and Progress* (Eds.: P. Diehl, E. Fluck, R. Kosfeld), Springer Publishers, Berlin, Heidelberg, New York, **1978**, p. 76 ff.

[15] For a detailed discussion of IR spectra of alkali metal tetrahydroborates see: *Gmelin, Handbuch der Anorganischen Chemie, Ergängungswerk zur 8. Auflage*, vol. 33, pp. 8−11. It should be noted that usually four bands are observed although only one IR-active vibration is to be expected for tetrahedral symmetry. The four bands result from the ν_3, $2\nu_4$, $\nu_2 + \nu_4$, and $2\nu_2$ vibrations.

[16] H. H. Giese, H. Nöth, W. Ponikwar, *Eur. J. Inorg. Chem.* **1999**, 1931−1937.

[17] M. Bremer, H. Nöth, W. Ponikwar, *Chem. Ber.* **1995**, *128*, 455−460.

[18] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98* (Revision A.7), Gaussian, Inc., Pittsburgh, PA, **1998**.

[19] A. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652; C. Lee, W. Yang, R. Parr, *Phys. Rev. B* **1988**, *37*, 785−789.

[20] R. Krishnan, J. S. Binley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650−654.

[21] F. Ramirez, R. Sarma, Y. F. Chaw, T. M. McCaffrey, J. F. Maracek, B. McKeever, D. Nierman, *J. Am. Chem. Soc.* **1977**, *99*, 5285−5289.

[22] R. Sarma, F. Ramirez, B. McKeever, Y.F. Chaw, J. F. Maracek, D. Nierman, T. M. McCaffrey, *J. Am. Chem. Soc.* **1977**, *99*, 5289−5295.

[23] V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum Press, New York, **1978**; V. Gutmann, U. Mayer, *Adv. Inorg. Radiochem.* **1975**, *17*, 189−223.

[24] H. Irving, R. J. P. Williams, *Nature* **1948**, *162*, 746−754

[25] H. Irving, R. J. P. Williams, *J. Chem. Soc.* **1953**, 3192−3210.

[26] M. Bremer, PhD Thesis, University of Munich, **1995**.

[27] *SMART*: Siemens Analytical Instruments, Version 5.1, Madison, **1995**.

[28] *SAINT*: Siemens Analytical Instruments, Version 5.1, Madison, **1996**.

[29] *SHELX97*: G. M. Sheldrick, University of Göttingen, **1997**.

[30] A. A. Gorbik, O. P. Carkin, *Russ. J. Inorg. Chem.* **1985**, *30*, 1711−1714.

[31] J. D. Dill, P. v. R. Schleyer, J. S. Binkley, J. A. Pople, *J. Am. Chem. Soc.* **1977**, *99*, 6159−617.

Received May 28, 2002
[I02273]