RUSSIAN CHEMICAL REVIEWS
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January 1975

Translated from *Uspekhi Khimii*, **44**, 3 - 16 (1975)

U.D.C. 541.44 : 543.42

Application of the NMR Method in the Study of Simple and Complex Hydrides of Light Metals

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The review discusses the results of studies on simple and complex hydrides of light metals by NMR, in particular the relation between the parameters of the NMR spectra and molecular structure, the formation of complexes by the hydrides and the stability of such complexes, as well as the characteristic features of the spectra of hydroborate systems.
The bibliography includes 101 references

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I. INTRODUCTION

The results of studies on simple and complex hydrides, in particular boron and aluminium hydrides, by the NMR method are discussed in the present review. In all the tables quoted the spin–spin coupling constants J are expressed in hertz units (Hz), the chemical shifts are given in parts per million (p.p.m.), the δH are relative to $Si(CH_3)_4$, and the $\delta^{11}B$ are relative to $BF_3.(C_2H_5)_2O$. To facilitate comparison, data obtained by different investigators relative to other standards have been recalculated relative to the standards quoted above in accordance with the formulae quoted in the literature[1-10]. The minus sign of δ corresponds to a shift of the signals to low fields relative to the standard. The discrepancies between the chemical shifts found by different workers are most probably due to the use of different solvents (see, for example, Refs. 11–13).

II. COMPOUNDS CONTAINING PYRAMIDAL GROUPS

1. Complexes of the Type $BH_3.L$

Table 1 presents the literature values of the chemical shifts and the constants J_{B-H} for borane complexes with different ligands containing electron donating atoms of Group V and VI elements (O, S, N, and P).

These results make it possible to infer the following changes in the NMR spectra of the donor and acceptor molecules on complex formation.

1. The resonance signals due to the nuclei of the electron-accepting molecules are as a rule displaced towards higher fields relative to the chemical shifts due to the same nuclei in the molecules of the free components. On the other hand, the signals due to the nuclei of the electron-donating molecules shift towards lower

fields. The increase of the shielding of the boron atom on formation of complexes of the type $BH_3.L$ can be explained by a decrease of the paramagnetic contribution to the shielding through the transfer of electrons from the donor to the unfilled p_z boron orbital and the change in the hybridisation of boron from sp^2 to sp^3. This is confirmed also by the value of the spin–spin coupling constant J_{B-H}. It has been shown[7,16] that the J_{B-H} increases from 81 to 136 Hz when boron passes from the sp^2- to the sp^3-state. For the complexes $BH_3.L$, J_{B-H} is in the range 90–106 Hz. On this basis, it was concluded[7,16] that the B–H bonds in the complexes are in a state of hybridisation intermediate between sp^2 and sp^3.

Table 1. The NMR parameters of borane complexes.

Compound	δ^{11} B	J_{B-H}	δ BH_3	δ CH_3	δ CH_2	$\delta CH_3 - \delta CH_2$	References
1	2	3	4	5	6	7	8
$(CH_3)_2O \cdot BH_3$	−2.5	104	—	−3.71	—	—	14,15
$(CH_2)_4O \cdot BH_3$	0.9	103	—		−4.00	—	8,14,15,16
$(C_2H_5)_2O \cdot BH_3$		134			−2.11	2.28	14
$(C_2H_5)_2O \cdot BHCl_2$	6	130	—	−1.28	−1.95	0.67	17
$(C_2H_5)_2O \cdot BCl_3$				−1.60	−4.84	3.24	14,18,19
$(CH_3)_2S \cdot BH_3$	20.1	—	—	—	—	—	15
$(CH_2)_4S \cdot BH_3$	20.1	—	—	—	—	—	15
$(CH_3)_3N \cdot BH_3$	8.1	96–98	−1.62	−2.58	—	—	15,16,20–26
$(CH_3)_2NH \cdot BH_3$	14.5	94–96	−1.46	−2.52	—	—	16,21,25,26
$CH_3NH_2 \cdot BH_3$	18.5	93–96	−1.32	−2.55	—	—	21,25,26
$NH_3 \cdot BH_3$	23.1	91–94	−1.29	—	—	—	21,26
$(C_2H_5)_3N \cdot BH_3$	13.4	—	−1.38	−1.13	−2.75	1.62	8,21,22
$(C_2H_5)_3N \cdot BH_2Cl$	1.7	—	—	—	—	—	27
$(C_2H_5)_3N \cdot BCl_3$	9.7	—	—	—	—	—	28
$(C_2H_5)_3N \cdot BH_2Br$	6.7	—	—	—	—	—	27
$(C_2H_5)_3N \cdot BBr_3$	5.4	—	—	—	—	—	8,28
$(C_2H_5)_3N \cdot BH_2I$	16.7	—	—	—	—	—	27
$(C_2H_5)_3N \cdot BI_3$	60.1	—	—	—	—	—	8,28
$(CH_3)_3P \cdot BH_3$	36.8	103–104	−0.44	−1.24	—	—	15,21,29–31
$(CH_3)_2PH \cdot BH_3$	37.4	90–96	−0.43	—	—	—	8,16,32
$CH_3PH_2 \cdot BH_3$	—	—	−0.53	—	—	—	31,33
$PH_3 \cdot BH_3$	42.5	103–104	−0.53	—	—	—	31,33
$PF_3 \cdot BH_3$	48.3	107	—	—	—	—	31
$PHF_2 \cdot BH_3$	42.1	103	—	—	—	—	31
$[(CH_3)_2N]_3P \cdot BH_3$	43	96	—	−2.63	—	—	29
$[(CH_3)_2N]_3P \cdot BH_2Cl$	21	124	—	−2.72	—	—	29
$[(CH_3)_2N]_3P \cdot BHCl_2$	6	144	—	−2.79	—	—	29
$[(CH_3)_2N]_3P \cdot BCl_3$	3	—	—	−2.84	—	—	29
$(CH_3O)_3P \cdot BH_3$	46	96	−0.33	−3.73	—	—	25,29,34,35
$(CH_3O)_3P \cdot BH_2Br$	30	131	—	−3.84	—	—	29
$(CH_3O)_3P \cdot BHBr_2$	21	142	—	−4.05	—	—	29
$(CH_3O)_3P \cdot BBr_3$	20	—	—	−4.16	—	—	29
$(C_2H_5)_3P \cdot BH_3$	42	96	−0.20	−1.12	−1.60	0.48	17,29
$(C_2H_5)_3P \cdot BH_2Cl$	20	115	—	−1.20	−1.82	0.62	17
$(C_2H_5)_3P \cdot BHCl_2$	6	131	—	−1.28	−1.95	0.67	17
$(C_2H_5)_3P \cdot BCl_3$	3	—	—	−1.32	−2.08	0.76	17
$(C_2H_5)_3P \cdot BH_2Br$	25	111	—	−1.23	−1.86	0.63	17
$(C_2H_5)_3P \cdot BHBr_2$	16	128	—	−1.31	−2.05	0.74	17
$(C_2H_5)_3P \cdot BBr_3$	15	—	—	−1.39	−2.21	0.82	17

2. Changes are observed in the chemical shifts of nuclei not directly involved in the formation of donor–acceptor bonds. These changes are smaller the more remote is the given atom from that involved in the formation of the coordinate bond. One may conclude that the donor–acceptor interaction alters the electronic structure of both donor and acceptor molecules. However, the electron density of the atoms in the α-position relative to those joined by the coordinate bond changes to the greatest extent.

In NMR studies on borane complexes much attention is devoted to the problem of the possible use of ^1H and ^{11}B chemical shifts as characteristics of the relative stabilities of the complexes. For example, the shielding of the boron nuclei in the acceptors and the deshielding of the nuclei forming part of the donor molecules (L) increase in the sequence $BF_3 < BCl_3 < BBr_3 < BI_3$ in the complexes BX_3 (X = halogen) with any ligands L[36–38]. This sequence of electron accepting capacities coincides with the sequence of the enthalpies of formation of boron halide complexes with pyridine[37,38]. It follows from the NMR data that the complex $BH_3.P(CH_3)_3$ is more stable than $BH_3.N(CH_3)_3$. This is explained by a shift[39] of the electrons in the B–H bonds to the 3*d* orbital of phosphorus. The hypothesis of the $d\pi - p\pi$ interaction in complexes with phosphines has not been confirmed. The shift of the electrons localised in the B–H bond should lead to a decrease of the hydrogen atom electron density and hence displace the signal to lower fields. In reality the opposite behaviour is observed in the ^1H spectra of $BH_3.P(CH_3)_3$ and $BH_3.N(CH_3)_3$: the chemical shifts of the protons in the B–H bonds are −0.44 and −1.62 p.p.m. respectively. The sequence of the changes in the NMR parameters is frequently inconsistent with the expectation based on the energy of the donor–acceptor interaction[21,23]. For example, a correlation is observed[21] between the number of methyl groups at the nitrogen atom in the complexes $BH_3.NH_{3-n}(CH_3)_n$ and the ^1H and the ^{11}B chemical shifts. Table 1 shows that, on passing from NH_3 to $N(CH_3)_3$, the signals are monotonically displaced towards lower fields. The change in the proton chemical shifts is evidence for a systematic increase of the *s*-character of the boron orbitals in the direction of hydrogen atoms with increase of the number of methyl groups at the nitrogen atom. The *s*-character of the fourth boron orbital and its capacity for donor–acceptor interaction should decrease in the same sequence. In such a case the ^{11}B chemical shifts should diminish on passing from $BH_3.NH_3$ to $BH_3.N(CH_3)_3$, which does in fact occur. However, this is inconsistent with the finding that borane–amine complexes are more stable than the complexes with ammonia[24].

The change in the electronegativity of the donor and acceptor atoms on complex formation is also indicated by the changes in the internal shifts of the protons of the ethyl groups linked to these atoms. A linear correlation between the electronegativity of X and the internal proton shift, expressed as the difference $\delta CH_3 - \delta CH_2$, has been established[40–43] for $(C_2H_5)_nX$. This correlation is also valid for molecules combined in a complex[22,44–46]. The internal proton shift in compounds of the type $(C_2H_5)_nX$, which behave as donors (X = O, S, N, or P), as a rule increases, while in compounds behaving as acceptors (X = metal) it decreases. Consequently the electronegativity of donor atoms increases on complex formation and that of acceptor atoms diminishes, in agreement with the decrease or increase of electron density at the atom X as a result of charge transfer from the donor to the acceptor. Thus the internal shifts of the protons in the ethyl groups decrease in the complexes $BH_nX_{3-n}.(C_2H_5)_3P$ (X = halogen)[17]. This means that the electron density at the phosphorus atom diminishes on complex formation. The internal shifts give rise to the following sequence of the electron-accepting capacities of boron compounds: $BBr_3 > BCl_3 > BHBr_2 > BHCl_2 > BH_2Br > BH_2Cl > BH_3$.[17] It is significant that this sequence is confirmed by the enthalpies of formation of the BBr_3, BCl_3, and BH_3 complexes with pyridine[37,38]:

Complex	$C_5H_5N \cdot BBr_3$	$C_5H_5N \cdot BCl_3$	$C_5H_5N \cdot BH_3$
$-\Delta H^\circ$ kcal mole^{-1}	32.0	30.8	28.8

Thus the study of the NMR spectra of borane complexes yields information about the nature of the changes in the electronic structures of the components of the complex. Bearing in mind the complexity of the dependence of the chemical shifts on a number of factors, definite $\Delta H^\circ - \delta$ relations can be expected only for series of compounds with similar structures.

2. Complexes of the Type $AlH_3.L$

Table 2 presents data for the proton chemical shifts in several aluminium complexes. Their analysis makes it possible to infer the following changes in the electronic structure of the donor and acceptor molecules on complex formation.

Table 2. The proton chemical shifts in the spectra of coordination compounds of aluminium hydride.

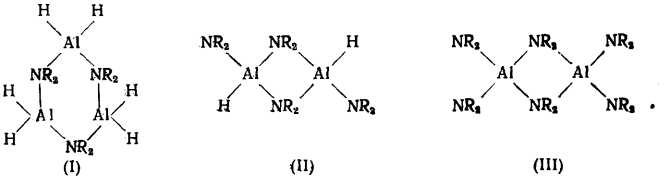
Compound	δ AlH	δ CH_3	δ CH_2	δ CH_2–X	References
$H_3Al\cdot OC_4H_8$	−4.08	−3.81 −1.43	—	—	47
$H_3Al\cdot N(CH_3)_3$	−3.81	—	—	−2.08	47–50
$H_3Al\cdot 2OC_4H_8$	−3.61	−4.13 −2.25	—	—	47
$H_3Al\cdot 2N(CH_3)_3$	−3.56	—	—	−2.25	47
$H_3Al\cdot 2O_2C_4H_8$	−3.56	−4.03	—	—	47
$H_3Al\cdot N(CH_3)_3\cdot OC_4H_8$	−3.56	−4.13 −2.25	—	−2.75	47
$H_3Al\cdot N(CH_3)_3\cdot O_2C_4H_8$	−3.56	−4.13	—	−2.75	47
$H_3Al\cdot OC_4B_8\cdot O_2C_4H_8$	−3.56	−4.1 −2.25	—	—	47
$H_3AlC_2H_5\cdot N(CH_3)_3$	−3.54	0.20	−0.97	−2.48	48
$HAl(C_2H_5)_2\cdot N(CH_3)_3$	—	0.15	−1.09	−2.38	48
$H_2AlCH_3\cdot N(CH_3)_3$	−3.54	—	0.80	−2.46	48
$HAl(CH_3)_2\cdot N(CH_3)_3$	—	—	0.83	−2.39	48
$HAlCl_2\cdot O(CH_3)_2$	−3.1	—	—	−3.9	51
$HAlCl_2\cdot O(C_2H_5)_2$	—	−4.41	—	−1.6	51
$HAlCl_2\cdot OC_4H_8$	−2.1	−3.6 −1.7	—	—	51
$H_3Al\cdot P(C_2H_5)_3$	−3.33	−1.71	−1.15	—	52
$H_2AlCl\cdot P(C_2H_5)_3$	—	−1.78	−1.18	—	52
$HAlCl_2\cdot P(C_2H_5)_3$	—	−1.82	−1.20	—	52
$AlCl_3\cdot P(C_2H_5)_3$	—	−1.96	−1.26	—	52

1. With increase of the coordination number (C.N.) of aluminium or with increase of the electron-donating capacity of the ligand for the same coordination number, the chemical shift of the protons linked directly to aluminium increases. This indicates an increase of electron density at the nuclei of the acceptor molecule, caused by charge transfer from the donor.

2. The NMR data for 1 : 1 and 1 : 2 complexes lead to the conclusion that the strength of the bond between aluminium and the ligand $N(CH_3)_3$ is greater than for OC_4H_8†, since the chemical shift of the hydride protons in $AlH_3.N(CH_3)_3$ is greater than in $AlH_3.OC_4H_8$. On formation of mixed 1 : 2 complexes, differences in the shielding of the H–Al protons are not observed. At the same time an excess of tetrahydrofuran (THF) is necessary for the addition of a second OC_4H_8 molecule to the complex $AlH_3.OC_4H_8$.[47]

3. No changes were observed in the chemical shifts of the protons of the CH_3 groups in the NMR spectra of the complex $AlH_3.N(CH_3)_3$ and therefore the state of the $N(CH_3)$ molecule changes only slightly on coordination. The free electron pair of the nitrogen atom in the $N(CH_3)_3$ molecule is involved in sp^3 hybridisation. If a coordinate bond is formed, there is no change in the valence state of carbon. On the other hand, in the complex $AlH_3.2OC_4H_8$ the proton resonance frequency in the α-CH_2 group decreases by 10 Hz, while the resonance frequency for β-CH_3 protons remains unchanged. This indicates alterations in the valence state of the oxygen atom. The NMR spectra of the complexes $H_{3-n}AlX_n.2OC_4H_8$ (n = 1, 2; X = Cl, Br, or I) indicate descreening of the protons in the α- and β-CH_2 groups in THF due to electron withdrawal from the oxygen atom to the aluminium atom[53]. The internal shift of the ethyl protons in the compounds $AlH_nCl_{3-n}.P(C_2H_5)_3$ increases[52] with increase of the degree of substitution of hydrogen atoms by chlorine. This change in the internal shift indicates an increase in electron-accepting capacity in the sequence $AlCl_3 > AlCl_2H > AlClH_2 > AlH_3$. Unfortunately the enthalpies of formation of these complexes are not available, which precludes their comparison with NMR data.

The structures of the above complexes in solution can change markedly as a result of association. The degree of association becomes more marked on passing to complexes with higher dipole moments and also on formation of hydrogen bond bridges of the type Al–H–Al or Al–H_2–Al. The existence of hydrogen bond bridges should have been reflected in the corresponding ^1H NMR shifts or should have given rise to additional signals. For complexes of aluminium hydride with trimethylamine, THF, and dioxane, not more than one signal due to the proton linked directly to the aluminium nucleus was observed[47]. The $R_2AlH.N(CH_3)_3$ and $RAlH_2.N(CH_3)_3$ complexes can undergo a different type of association via the methyl group for R = CH_3 and via the methylene group for R = C_2H_5. This follows from the splitting of the lines in the ^1H NMR spectra of these compounds in cyclohexane[48]. Moreover the formation of the dimer $Al_2(C_2H_5)_6$ does in fact proceed via the CH_3 group, which has also been confirmed by NMR. The ^1H NMR spectra of amino-aluminium hydrides of the type $H_{3-n}Al(NR_2)_n$ (n = 1, 2, or 3; R = CH_3 or C_2H_5) have been investigated[54]. It was shown that in benzene solutions association takes place via the formation of Al–N–Al linkages and the most probable structures (I)–(III) were proposed:



(I) (II) (III)

The formation of bridged structures is confirmed by the presence in the ^1H NMR spectra of two signals due to NR_2 with both R = CH_3 and R = C_2H_5. Infrared spectroscopic data are consistent with those derived from ^1H NMR.[54] The association of complexes of the type $AlF_nCl_{3-n}.THF$ (n = 1 or 2) proceeds via the fluorine atoms[55].

Thus the chemical shifts and the spin–spin coupling constants yield information about the changes in the distribution of electron density, about the capacity for hybridisation, and about the amount of ionic character of the bonds when the molecules are bound in a complex.

III. COMPOUNDS CONTAINING TETRAHEDRAL GROUPS

Table 3 presents the ^{11}B NMR parameters for certain ionic hydroborates.

The ^1H NMR spectrum of an aqueous solution of $NaBH_4$ contains a quartet with the relative intensities 1 : 1 : 1 : 1 and a weak septet[58–61]. In the ^{11}B NMR spectrum there is a 1 : 4 : 6 : 4 : 1 quintet. The fine structure of the spectrum was determined using double resonance. On irradiation of the boron nucleus, the initial quartet is converted into a single line. This indicates the equivalence of all the protons in the BH_4^- anion and their interaction with ^{11}B.

† OC_4H_8 = THF.

Such equivalence is possible if the tetrahydroborate ion has a square planar, pyramidal, or tetrahedral structure. The first two models should lead to relatively more marked variation of the electric field gradients at the boron atom with the angle and this should be reflected in a broadening of the ^1H NMR lines. Narrow lines in the quartet are observed experimentally, which implies that the tetrahydroborate ion is most likely to have the tetrahedral structure. The boron chemical shifts for $LiBH_4$ depend, according to Ehemann et al.,[57] on the concentration of the solution and the type of solvent, i.e. apparently on the degree of separation of the cation and anion due to solvation effects.

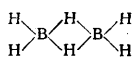
Table 3. The ^{11}B NMR parameters of certain ionic tetrahydroborates.

Compound	Solvent	$\delta^{11}B$	J_{B-H}	References
$NaBH_4$	0.1 *N* NaOH	43.8	81	16
$LiBH_4$	Ether	38.2	75	56
$[(C_4H_9)_4N]BH_4$	THF	37.7	82	57
$[(C_{18}H_{17})NC_3H_7]BH_4$	Benzene	36.9	82	57

IV. COVALENT HYDROBORATES WITH BRIDGE BONDS

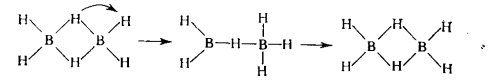
1. Diborane and Its Derivatives

It has been established by electron diffraction[62] and infrared spectroscopy[63,64] that the electron-deficient diborane molecule has a bridged structure:

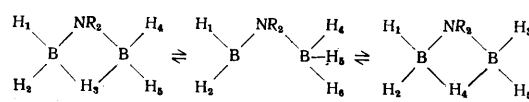


In this structure four hydrogen atoms are linked directly to the boron atoms by the usual covalent two-electron bonds, while the remaining two hydrogen atoms occupy bridging positions, saturating the remaining valences of the boron atoms. The ^1H and ^{11}B NMR spectra of liquid diborane are consistent with the bridged model[32,37,61,64-67]. Thus the ^{11}B NMR spectrum at $f = 30$ MHz contains one multiplet consisting of a triplet of triplets[32]. The major triplet splitting arises in consequence of the spin–spin interaction of the boron nuclei with the two equivalent terminal protons and the minor splitting is due to the interaction of the boron atom with the pair of bridge hydrogen atoms. An additional confirmation of the bridged structure of B_2H_6 is provided by its ^1H NMR spectrum, from which the existence of two different types of protons follows directly. At a frequency of 30 MHz the ^1H NMR spectrum consists of a complex multiplet. The interpretation of this spectrum shows to a first approximation that the observed component lines have the following origins: a quartet corresponds to the terminal hydrogen atoms linked to one ^{11}B atom ($I = 3/2$) while a septet corresponds to the bridge hydrogen nuclei linked to the two boron nuclei. When the interaction with the boron nuclei is suppressed by double resonance, the two different types of protons are represented in the ^1H NMR spectrum by two singlets with the area ratio 2 : 1. The signals due to the hydrogen nuclei linked to ^{10}B ($I = 3$) form a weak septet. The bridge protons resonate in a higher field than the terminal protons. This shows that the B–H–B linkage is more ionic than B–H. This is also indicated by the ratio of the spin coupling constants. Overall, the NMR parameters show that the electron cloud density at the bridge protons is higher than at the terminal protons. The results of a quantum-mechanical calculation of the magnetic shielding of protons in diborane are consistent with this conclusion[68]. Subsequently the NMR spectra of liquid diborane were investigated on spectrometers with a higher working frequency and with a higher resolving power[66,67]. With increase of the working frequency, the centres of the multiplets are separated and the interpretation of the spectrum is simplified. In addition, the increase in the resolving power of the apparatus made it possible to observe more remote spin–spin interactions of the nuclei in the diborane molecule. According to modern ideas, the spin system of B_2H_6 belongs to the type $A_2A'_2M_2XX'$, in which the two boron nuclei (X and X′) are magnetically nonequivalent owing to the different degrees of spin–spin interaction with the terminal protons (A_2, A'_2).

There are solvents in which the terminal and bridge protons appear to be magnetically equivalent, for example the spectrum of diborane in ethyl ether at −26°C consists of a triplet of triplets, the structure of the spectrum changes with increase of temperature, and at 84°C a septet is observed[69]. In the ^{11}B NMR spectrum of diborane in the dimethyl ether of ethylene glycol a septet is observed at room temperature. The authors explain the equivalence of the protons by rapid intramolecular exchange via the following scheme:



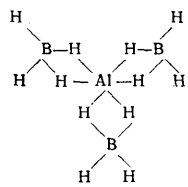
In this scheme the unstable intermediate species may be stabilised by interaction with a solvent molecule, which behaves as an electron donor. The ^{11}B NMR spectra of the products of the reactions of diborane with inorganic and organic anions indicate the formation of substituted hydroborate anions[70-73]. According to Geines and Schaeffer[26], the chemical shifts of the boron nuclei in the aminodiboranes $B_2H_5NH_2$, $B_2H_5NHCH_3$, and $B_2H_5N(CH_3)_2$ are respectively 26.7, 22.7, and 17.0 p.p.m., i.e. the signals shift towards lower fields with increase of the number of methyl groups at the nitrogen atom. Phillips et al.[16] observed that, on raising the temperature from −10° to 40°C, the ^{11}B resonance lines in the $B_2H_5N(CH_3)_2$ spectrum are broadened and the splitting into doublets almost vanishes. The authors explained the breakdown of the spin–spin interaction of boron with the bridge protons by partial dissociation of the B–H–B linkage with subsequent rotation of the BH_3 group about the B–N bond and the formation of a new B–H–B linkage involving a different hydrogen atom. As a result, all the protons become equivalent:



Williams et al.[74] investigated the ^{11}B NMR spectra of various methyldiboranes and their deuterio-derivatives. Their results show that the replacement of hydrogen by a methyl group shifts the ^{11}B signal to a lower field. A more detailed analysis of the ^1H NMR spectra of these compounds is described in the literature[75-77].

2. Aluminium Tetrahydroborate

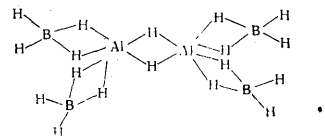
In the aluminium tetrahydroborate structure, proposed on the basis of electron diffraction studies[78] and infrared spectra[79], the aluminium atom is located at the centre of an equilateral triangle formed by the boron atoms. Four hydrogen atoms are linked to each boron atom, so that the latter is in a tetrahedral environment. Two of these hydrogen atoms form bridges between the boron atoms and aluminium, i.e. there are two types of protons in the molecule (bridge and terminal protons):



The ^1H and ^{11}B NMR spectra of aluminium tetrahydroborate were first examined by Ogg and Ray[80]. The ^1H NMR spectrum at a frequency of 30 MHz consists of an unresolved multiplet with a line half-width of about 300 Hz. The spectrum was interpreted using the double resonance of aluminium and boron nuclei. On irradiation of the boron nucleus, the resonance line in the proton spectrum becomes somewhat narrower, although it still remains fairly broad (220 Hz). Irradiation of the aluminium nucleus leads to the appearance in the spectrum of a quartet with a splitting of 87 Hz, as for the BH_4^- ion. The ^{11}B NMR spectrum shows a quintet with the intensity ratios 1 : 4 : 6 : 4 : 1, the splitting and positions of which are characteristic of the BH_4^- ions. In the ^{27}Al NMR spectrum there is an unresolved multiplet due to the spin–spin interaction of the aluminium nucleus with the twelve equivalent protons[81]. Interpretation of the NMR spectra of aluminium tetrahydroborate leads to the following conclusions concerning its structure in the liquid phase. Firstly, all the hydride protons in the molecule have the same electronic environment, i.e. they are "chemically equivalent". Secondly, all the protons are linked to both boron and aluminium. The initial broad line in the proton spectrum can be interpreted as a multiplet consisting of 24 lines due to the spin–spin coupling with boron ($I = 3/2$) and aluminium ($I = 5/2$), the components of the multiplets being appreciably broadened owing to the quadrupole relaxation of the aluminium nucleus. Thirdly, each boron nucleus is linked to four equivalent protons. The narrow lines in the ^{11}B NMR quintet indicate a nearly tetrahedral disposition of the protons around the boron atom. These conclusions do not lead to an unambiguous confirmation of the bridged model of aluminium tetrahydroborate proposed on the basis of infrared spectroscopic and electron diffraction studies. The ^1H NMR spectrum of this structure should contain signals due to two types of protons, while in reality all the protons give rise to one common signal. This apparent contradiction can be eliminated by assuming that there is a dynamic process leading to the exchange and averaging of the bridge and terminal protons over a period of time. To elucidate the mechanism of proton exchange in $Al(BH_4)_3$, Ogg and Ray[80] studied the NMR spectra of liquid specimens at temperatures ranging from −40 to 60°C. The spectra of deuterio-derivatives of aluminium tetrahydroborate were investigated and it was shown that the form of the proton spectrum hardly changes with temperature. Deuteriation leads to a broadening of the quartet components in the ^1H NMR spectrum obtained on single irradiation of the aluminium nucleus. These results led the authors to the conclusion that the proton exchange in aluminium tetrahydroborate is non-classical (there is a tunnel effect)[80]. The same investigators showed that at 80°C $Al(BH_4)_3$ undergoes reversible dissociation:

$$2Al(BH_4)_3 \rightleftharpoons Al_2B_4H_{12} + B_2H_6 .$$

A dimeric structure was proposed for $Al_2B_4H_{12}$:



The ^1H NMR spectrum of $Al_2B_4H_{12}$ contains a quartet, in contrast to the broad signal of $Al(BH_4)_3$. It was suggested that the fine structure of the spectrum is due to the rapid rotation of the BH_4 groups, which interferes with the spin–spin interaction between the protons and the aluminium nucleus. The broad signal in the ^1H NMR spectrum of $Al(BH_4)_3$ is converted into a quartet when the temperature of the liquid specimen is raised from −40 to 90°C; this change can be both reversible and irreversible[81]. The authors attribute the observed changes to exchange between two possible structural models of the $Al(BH_4)_3$ molecule—prismatic and octahedral. However, in order to confirm this conclusion, it is necessary to study the kinetics of the transition from one form to the other and also each of these forms in the solid phase.

Table 4. The ^1H and ^{11}B NMR parameters of certain covalent metal tetrahydroborates.

Compound	δ ^{11}B	δ H	J_{B-H}	References
$Mg(BH_4)_2$	42.8	—	83.5	57
$Al(BH_4)_3$	37	−1.50	86	83,84
$Be(BH_4)_2$	34.6	—	84.2	57
$CuBH_4 \cdot P(C_6H_5)_3$	30	—	84	
$Ti(BH_4)_3 \cdot O(C_2H_5)_2$	23	—	—	57
$Hf(BH_4)_4$	14.2	−2.85	90	85,86
$Zr(BH_4)_4$	11.0	−1.58	90	85,86
$Th(BH_4)_4$	8.0	—	86.6	57
B_2H_6	−17.5	−3.92 0.56	135 46	76
$UBH_4(C_5H_5)_3$	−64.0	−74.23	86	87

Williams[82] notes that the occurrence of internal exchange is characteristic not only of aluminium tetrahydroborate but also of many other boron hydrides and their complexes with Lewis bases. The observed equivalence of the protons has been explained by a tautomeric transition in the liquid phase between structures with one and two bridge bonds via hydrogen atoms[82]:

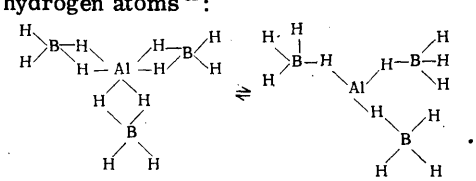


Table 4 presents the results of studies on certain covalent metal tetrahydroborates by NMR.

The observed differences between the ^1H and ^{11}B chemical shifts can probably be explained by differences between the electronic structures of the central atoms. However, the NMR spectra of all these compounds indicate the equivalence of the protons. The disappearance of the fine structure from the ^1H NMR spectrum of $Zr(BH_4)_4$, observed when the temperature is reduced, was explained[88] by the retardation of the intramolecular exchange. However, even at the lowest temperatures it was impossible to ensure the localisation of protons. It has been shown[89] that the observed temperature variation of the spectra of zirconium and hafnium tetrahydroborates is due to the influence of the quadrupole relaxation of the boron nuclei on the resonance of the protons linked directly to these atoms. On the whole, one may say that the studies on covalent tetrahydroborates with bridge bonds by NMR make it possible to draw inferences concerning the bond between the BH_4 group and the central atom and also concerning the mobility of the protons. Diborane is apparently the only example of compounds of this class whose ^1H NMR spectrum shows separate signals due to bridge and terminal protons.

V. COVALENT TETRAHYDROBORATES CONTAINING AN M–L COORDINATE BOND

Table 5 presents the NMR parameters for the $Al(BH_4)_3$ complexes with $N(CH_3)_3$, $P(CH_3)_3$, $As(CH_3)_3$, $O(CH_3)_2$, $S(CH_3)_2$, and $O(C_2H_5)_2$ as well as complexes with hydride derivatives of $Al(BH_4)_3$. The ^{11}B NMR spectra of all these compounds contain a quintet, showing that four identical protons are linked to each boron atom and that all the boron atoms are equivalent in derivatives containing two or more tetrahydroborate groups[84,90]. The presence of four identical protons linked to boron limits the number of possible structures involving the B–N and Al–N–B bridge bonds. The ^1H NMR spectrum of the tetrahydroborate group consists of a broad unresolved signal without the expected fine structure due to the spin–spin interaction of protons with boron and aluminium. However, significant differences between the hydride proton absorption line forms are observed for some of the compounds. For example, the ^1H NMR spectra of the tetrahydroborate group in the complexes with $As(CH_3)_3$ and $S(CH_3)_2$ are split into four lines owing to the spin–spin interaction with boron, while interaction with aluminium is not observed[84]. It has been noted that the proton spectrum of the complex $Al(BH_4)_3.N(CH_3)_3$ contains a multiplet comprising twelve lines, due to the interaction of the protons with boron and aluminium and $J_{B\text{-}H} \simeq 2J_{Al\text{-}H}$.[83,84] There is splitting also in the ^{27}Al NMR spectrum of this compound. The observed differences between the proton spectra of the above compounds can probably be accounted for by the effect of the quadrupole relaxation of the aluminium nucleus. Evidently the electric field gradient at the ^{27}Al nucleus in the complex with $N(CH_3)_3$ is smaller and the rate of relaxation of this nucleus in the compounds with $As(CH_3)_3$ and $S(CH_3)_2$ is much higher than in all the other complexes examined. Thus, using the available information about the absorption line form in the NMR spectra, complexes of the type $Al(BH_4)_3.L$ can be arranged in the following sequence in terms of increasing asymmetry of the electronic environment of the aluminium nucleus:

$$N(CH_3)_3 < P(CH_3)_3 < As(CH_3)_3$$
$$O(CH_3)_2 < S(CH_3)_2$$

At elevated temperatures the signal due to amino-group protons in the ^1H NMR spectrum of $Al(BH_4)_3.N(CH_3)_3$ is split[92], which is associated either with a marked orientation of the ligand in the complex or with the existence of the equilibrium:

$$2Al(BH_4)_3 \cdot N(CH_3)_3 \rightleftharpoons Al(BH_4)_3 \cdot 2N(CH_3)_3 + Al(BH_4)_3 .$$

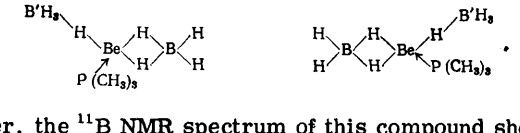
If it is assumed that there is an equilibrium between the 1 : 1 and 1 : 2 complexes, the singlet at −60°C can be attributed to the undissociated form and the two signals at 60°C to the existence of two equilibrium forms of the complex. With decrease of temperature, the components of the multiplet due to the tetrahydroborate protons are broadened, which has been explained[88] by the retardation of proton exchange. However, such spectral changes can be attributed also to the influence of the quadrupole NMR relaxation of boron and aluminium.

Table 5. The ^1H and ^{11}B NMR parameters of aluminium tetrahydroborate complexes.

Compound	^{11}B NMR		^1H NMR				References
	δ ^{11}B	J_{B-H}	δ BH_4	δ CH_3	δ CH_2	J_{B-H}	
$Al(BH_4)_3 \cdot P(CH_3)_3$	35.5	87	−0.63	−0.93	—	87	84
$Al(BH_4)_3 \cdot As(CH_3)_3$	35.6	88	−0.91	−0.97	—	87	84
$Al(BH_4)_3 \cdot O(CH_3)_2$	—	—	−0.70	−3.23	—	—	84
$Al(BH_4)_3 \cdot S(CH_3)_2$	—	—	−0.77	−1.85	—	—	84
$Al(BH_4)_3 \cdot O(C_2H_5)_2$	35.7	85	−0.48	−1.23	−3.15	—	84
$Al(BH_4)_3 \cdot N(CH_3)_3$	37.8	88	−0.73	−0.64		87	81,84
$Al(BH_4)_2H \cdot N(CH_3)_3$	38.2	85	—	—	—	—	90
$AlH_2BH_4 \cdot N(CH_3)_3$	38.4	85	—	—	—	—	90
$Al(C_2H_5)_2BH_4 \cdot N(CH_3)_3$	39.4	85	0.08	−2.40 0.91	— 0.10	84	91

Among complexes of aluminium tetrahydroborate with ammonia, a study has been made on the compound with the empirical formula $Al(BH_4)_3.6NH_3$. The ^1H NMR spectrum in ammonia shows[93] a single quartet characteristic of BH_4^-. This spectrum probably agrees best with the ionic structure $[Al(NH_3)_6^{3+}](BH_4)_3^-$. However, the study of ^{11}B NMR spectra suggested another possible structure[94,95]: $AlH_2(NH_3)_4^+BH_2(NH_3)_2^+(BH_4)^-$. The true structure of this compound still has to be determined.

The beryllium complexes $Be(BH_4)_2.L$, where L = $O(C_2H_5)_2$, $P(CH_3)_3$, or $N(CH_3)_3$, were also studied by NMR.[96] The NMR spectra of all these compounds demonstrate the equivalence of both the protons and boron atoms. The following possible structures have been proposed for $Be(BH_4)_2.P(CH_3)_3$ on the basis of infrared spectra[97]:



However, the ^{11}B NMR spectrum of this compound show a single quintet (1 : 4 : 6 : 4 : 1), which demonstrates the equivalence of both the hydrogen atoms and ^{11}B atoms. The authors believe that the above forms can be rapidly interconverted so that average signals due to B and B′ atoms are observed.

The examples discussed show that the occurrence of proton exchange is characteristic not only of free metal tetrahydroborates but also of their neutral complexes.

VI. MIXED METAL HYDRIDES

The NMR method has been widely used to investigate the products of the various double decomposition reactions. For example, the study of the ^{1}H and ^{11}B NMR spectra of products of the reaction between lithium salts and aluminium tetrahydroborate established[57,93,94] that the complex anion $[Al(BH_4)_4]^-$ is formed. The ^{11}B NMR spectrum of this anion shows a quintet (1 : 4 : 6 : 4 : 1) and the ^{1}H NMR spectrum consists of a broad unresolved signal. The infrared spectra indicate a bridged structure, while the NMR spectra demonstrate the equivalence of all the protons. There is probably proton exchange in the anion $[Al(BH_4)_4]^-$, as in $Al(BH_4)_3$.

The formation of two complex beryllium anions, $Be(BH_4)_3^-$ and $Be_2(BH_4)_5^-$, has been reported[98]. A structure with a formally tricoordinate beryllium atom was proposed for $Be_2(BH_4)_5^-$:

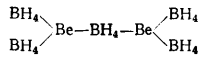


Table 6. The ^{11}B NMR parameters of certain mixed hydrides.

Compound	Solvent	δ ^{11}B	J_{B-H}	References
$LiTh(BH_4)_5$	Ether	13.4	84.5	100
$LiZr(BH_4)_5$	Ether	13.5	86	100
$LiHf(BH_4)_5$	Ether	15.4	86	100
$[(C_{16}H_{17})_3NC_5H_7][Al(BH_4)_4]$	Benzene	33.1	79	98
$[(C_{16}H_{17})_3NC_5H_7][Be(BH_4)_3]$	Benzene	34.7	80	98
$[(C_{16}H_{17})_3NC_5H_7][Be_2(BH_4)_5]$	Benzene	35.1	83	98
$LiZn(BH_4)_3$	Ether	42.3	84.5	101

The ^{11}B NMR spectra indicate the equivalence of all the tetrahydroborate groups. Table 6 presents the NMR parameters for certain mixed hydrides. The differences between the ^{11}B chemical shifts in the spectra of the above compounds are due to differences between the electronic structures of the central atoms, but all the spectra demonstrate the equivalence of the protons[99].

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