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Covalent Tetrahydroborates

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The properties, structure, and methods of preparation of the tetrahydroborates of beryllium, aluminium, and certain heavy metals (zirconium, hafnium, thorium, and uranium) are reviewed.
These compounds, which can provisionally be grouped together as the so-called covalent complex hydroborates, have much in common both as regards physical properties and high reactivity and as regards the nature of the chemical bond and the character of the chemical changes in which the $M(BH_4)_n$ molecules participate. The main types of chemical reactions of the covalent tetrahydroborates, the structural principles lying at the basis of their molecular and crystal structures, and also the possibility of using covalent tetrahydroborates in various fields of inorganic synthesis are examined. 114 references.

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I. INTRODUCTION

For the last 15—20 years the saltlike alkali metal tetrahydroborates, the crystal lattices of which contain isolated tetrahedral BH_4^- ions, have been the subject of an intensive investigation, which has shown the possibility of their use in preparative inorganic chemistry and chemical technology.

Considerably less attention has been paid to the tetrahydroborates of metals, the "cations" of which show high reduced moments z/r (beryllium, aluminium, and the heavy metals zirconium, hafnium, thorium, and uranium), where z is the charge and r the radius of the ion.

Evidently, the main reason for ignoring the experimental chemistry of the complex covalent tetrahydroborates of the $M(BH_4)_n$ type was the difficulties associated with the preparation and investigation of these extremely reactive and volatile compounds.

Actually, aluminium tetrahydroborate $Al(BH_4)_3$, for example, reacts explosively in the solid, liquid, and gaseous states with atmospheric oxygen and moisture, beryllium tetrahydroborate $Be(BH_4)_2$ and uranium tetrahydroborate $U(BH_4)_4$ are spontaneously inflammable in air, and so forth.

The relatively low thermal stability of the covalent tetrahydroborates (they all decompose rapidly and irreversibly in the range 130—150°C) gives rise to additional difficulties in their preparation.

Nevertheless the chemistry of the complex covalent hydroborates is much richer and more interesting than that of the saltlike tetrahydroborates. The $M(BH_4)_n$ molecules exhibit a dual reactivity: the BH_4 group in them is simultaneously a carrier of the functions of both a tetrahedral BH_4^- "ion" and an H_2BH_2 bridging group, close in structure and properties to the H_2BH_2 group in the diborane molecule.

The saltlike nature of the tetrahydroborates $M(BH_4)_n$ increases in the sequence:

	$Be(BH_4)_2$	$Al(BH_4)_3$	$U(BH_4)_4$	$Zr(Hf)(BH_4)_4$	$U(BH_4)_3$	$Ca(BH_4)_2$
z/r	4.4	4.3	3.8	3.7	2.8	2.0

It is interesting to trace how the structure of the BH_4 group situated in the field of the "cation" M and the type of the M—H—B chemical bond vary as the reduced moment z/r is increased.

In the most saltlike tetrahydroborate (that of U^{III}) the proper symmetry of the BH_4 group is evidently the same as in the tetrahydroborates of univalent cations, T_d. On going to molecular structures with $z/r > 3$ the nature of the bonding of the BH_4 group with the cation is more complicated. In the M^{IV} tetrahydroborates the symmetry of the BH_4 group is decreased to C_{3v} and a new type of multicentre bridging bond MH_3B, unknown in the chemistry of the boron hydrides, is formed.

The $Al(BH_4)_3$ molecule contains AlH_2B bridges close in structure to the BH_2B fragments in the B_2H_6 molecule (symmetry of the BH_4 group C_{2v}) and from the nature of the chemical bond in it is a complete analogue of diborane.

The $Be(BH_4)_2$ molecule, the structure of which is considered in detail on p. 5, can be described as the result of "association" of a distorted B_2H_6 molecule and a BeH_2 molecule[1] or as a combination of two BH_4 tetrahedra with a common vertex and a planar BeH_3 group, which complete a six-membered ring $\{BeH_3B_2\}$.[2]

The dual reactivity of the tetrahydroborates $M(BH_4)_n$ connected with the intermediate nature of the bond between the BH_4 group and the M atoms, appears clearly in the chemistry of aluminium tetrahydroborate, which reacts with alkenes like diborane and with ammonia like the tetrahydroborate $[Al(NH_3)_6](BH_4)_3$.[3,4]

Since the covalent tetrahydroborates, like diborane, are electron-deficient compounds—the number of atomic orbitals in the $M(BH_4)_n$ molecules is greater than the number of valency electrons—a specific type of reaction, not characteristic of the saltlike tetrahydroborates, is inherent for them. This refers to the addition of molecules which are donors of electrons, with the formation of new molecular structures of the type $M(BH_4)_n.mL$ (I) or $[M(BH_4)_nX]^-$ (II), in which the atom M, which exhibits a coordination number anomalously high from the viewpoint of classical ideas, is at the centre of a coordination polyhedron with an unusual configuration.

Examples of such compounds are the complexes[4,5] of aluminium tetrahydroborate with trimethylamine, trimethylphosphine, and trimethylarsine, in the molecules of which the aluminium atom is surrounded by three boron atoms, six hydrogen atoms, and a nitrogen atom, situated at the vertices of greatly distorted [H---AlH_5---N] pentagonal bipyramids.

The structures of compounds of types (I) and (II) are of exceptional interest in connection with the definition of the concepts of "valency" and "coordination" number, the classical treatment of which is inapplicable for the description of most light metal hydrides.

The prospects of the practical use of the tetrahydroborates $M(BH_4)_n$ is evidently linked with their use as starting materials in the preparation of new inorganic compounds containing an M—H—B bond and also with their high volatility and with the possibility of their use in this connection for separating elements with very similar properties, for example, Zr and Hf or the isotopes ^{235}U and ^{238}U.[6-10]

It has also been noted repeatedly[7,8] that the light metal tetrahydroborates, which have high heats of combustion, can be regarded as promising components of rocket fuels.

II. METHODS OF SYNTHESIS

1. DOUBLE DECOMPOSITION BETWEEN METAL HALIDES AND ALKALI METAL AND ALUMINIUM TETRAHYDROBORATES

Schlesinger[11,12] was the first to use the method of double decomposition for obtaining aluminium and beryllium tetrahydroborates from the corresponding chlorides and alkali metal tetrahydroborates by the reactions:

$$BeCl_2 + 2LiBH_4 \xrightarrow{140^\circ} Be(BH_4)_2 + 2LiCl\ , \quad (1)$$

$$AlCl_3 + 3MBH_4 \xrightarrow{100-130^\circ} Al(BH_4)_3 + 3MCl\ . \quad (2)$$

Reactions (1) and (2) take place in the solid phase at 100—130°C, the yield of the desired product depending on the ratio of the reagents and the nature of the tetrahydroborate used. It has been shown[12,13] that the greatest yield of aluminium and beryllium tetrahydroborates (90—95%) occurs when the metal chlorides react with lithium tetrahydroborate in ratios close to stoichiometric. When sodium tetrahydroborate is used the yield is considerably less (~50%), but the yield of aluminium tetrahydroborate can be increased by the introduction of a large excess of the metal chloride into the reaction mass[11,12]. When potassium tetrahydroborate is used, the yield of aluminium and beryllium tetrahydroborates by reactions (1) and (2) are reduced almost to zero.

However, when potassium tetrahydroborates reacts with aluminium chloride in the presence of lithium chloride the yield of aluminium tetrahydroborate is increased to 40—50%.[14] In addition to the main products from reactions (1) and (2), side-products are formed: diborane, hydrogen, and chloro-substituted derivatives of tetrahydroborates of composition $MCl_x(BH_4)_{n-x}$.[11,15]

Reaction (2) can also be effected in the presence of inert organic substances: petroleum, mineral oil, heavy mineral oil with graphite flakes, benzene; this facilitates the charging of the reagents, the mixing of the reaction mass, and the discharge of the product[16-20].

Lithium tetrahydroborate reacts with zirconium(IV) chloride in a manner similar to reactions (1) and (2):

$$ZrCl_4 + 4LiBH_4 \rightarrow Zr(BH_4)_4 + 4LiCl\ . \quad (3)$$

The yield of zirconium tetrahydroborate by reaction (3) is 77%; when sodium or potassium tetrahydroborate replaced the lithium salt zirconium tetrahydroborate could not be obtained by this method[21].

For uranium tetrahydroborate the "dry" method of synthesis—heating mixtures of alkali metal tetrahydroborates with uranium(IV) fluoride up to 200°C—did not give results. Uranium and thorium tetrahydroborates were obtained by the reaction of uranium(IV) and thorium(IV) fluorides with aluminium tetrahydroborate[22-24]:

$$MF_4 + 2Al(BH_4)_3 \rightarrow 2AlF_2BH_4 + M(BH_4)_4\ . \quad (4)$$

When there is an excess of aluminium tetrahydroborate the yield of uranium tetrahydroborate reaches 80%.[22,23] The method can also be used for the preparation of zirconium tetrahydroborate:

$$ZrCl_4 + 2Al(BH_4)_3 \rightarrow 2AlCl_2BH_4 + Zr(BH_4)_4\ . \quad (5)$$

However, in this instance there are additional difficulties associated with the separation of the reaction products, the volatilities of which are very similar. Zirconium and hafnium tetrahydroborates can be obtained from aluminium tetrahydroborate and fluoro-complexes[24,25]:

$$NaMF_5 + 2Al(BH_4)_3 \rightarrow NaF + 2AlF_2BH_4 + M(BH_4)_4\ . \quad (6)$$

Fluoro-complexes are used because zirconium(IV) and hafnium(IV) fluorides do not react directly with aluminium tetrahydroborates[26].

2. REACTION OF METAL ALKYLS OR METAL HYDRIDES WITH DIBORANE

The first covalent tetrahydroborate obtained by the reaction of a metal alkyl with diborane was that of aluminium[27,28]:

$$Al(CH_3)_3 + 2B_2H_6 \rightarrow Al(BH_4)_3 + B(CH_3)_3 . \quad (7)$$

The yield of the reaction was 70—80%. This method is also applicable for the preparation of beryllium tetrahydroborate[29].

Reaction (7) is inconvenient preparatively since it is slow, with the formation of intermediate products of the $Al(BH_4)_x(CH_3)_{3-x}$ type, which are difficult to separate.

Beryllium tetrahydroborate can also be obtained by the action of diborane on beryllium hydride[30]. There is a report of the possibility of obtaining aluminium tetrahydroborate in yields of up to 90% by the action of diborane on crystalline lithium tetrahydroaluminate at 70—80°C:[31]

$$LiAlH_4 + 2B_2H_6 \rightarrow LiBH_4 + Al(BH_4)_3 . \quad (8)$$

3. PREPARATION IN THE PRESENCE OF SOLVATING SOLVENTS

Fuchs and Kollonitsch[32,33] described the preparation of aluminium tetrahydroborate from calcium tetrahydroborate and aluminium chloride in tetrahydrofuran (THF) solution:

$$3Ca(BH_4)_2 + 2AlCl_3 \cdot C_4H_8O \xrightarrow{C_4H_8O} 3CaCl_2 + 2Al(BH_4)_3 \cdot C_4H_8O . \quad (9)$$

When the solution is cooled to −60°C a complex of aluminium tetrahydroborate and tetrahydrofuran crystallises from it.

Complexes of aluminium tetrahydroborate with diethyl ether are formed by the reactions[31,34]:

$$4AlH_3 \cdot Et_2O + 3BCl_3 \xrightarrow{Et_2O} Al(BH_4)_3 \cdot Et_2O + 3AlCl_3 \cdot Et_2O , \quad (10)$$

$$3LiAlH_4 + 3BCl_3 \xrightarrow{Et_2O} Al(BH_4)_3 \cdot Et_2O + LiCl + 2AlCl_3 \cdot Et_2O , \quad (11)$$

$$2AlH_3 \cdot Et_2O + nB_2H_6 \xrightarrow{Et_2O} 2H_{3-2n}Al(BH_4)_{2n} \cdot Et_2O . \quad (12)$$

The reaction of uranium(IV) fluoride with lithium tetrahydroborate in diethyl ether gives a complex of uranium tetrahydroborate with the ligand-solvent[22]. It is noteworthy, however, that the oxonium complexes of the covalent tetrahydroborates are stable compounds from which the non-solvated tetrahydroborates cannot be separated.

The methods of synthesis considered in sections II. 2 and II. 3 are preparatively inconvenient or associated with the impossibility of using difficulty available and costly initial substances. The most promising methods of preparation of the covalent tetrahydroborates are those based on double decomposition between metal halides and alkali metal or aluminium tetrahydroborates.

III. PHYSICOCHEMICAL PROPERTIES AND REACTIVITY

Under normal conditions the covalent tetrahydroborates $M(BH_4)_n$ are crystalline, except for aluminium tetrahydroborate, which is a colourless, mobile, low-boiling liquid.

Table 1 gives some physicochemical properties of the tetrahydroborates $M(BH_4)_n$.

In addition, the following quantities have been determined for liquid aluminium tetrahydroborate[35-37]: (a) coefficient of viscosity 2.0 mP (25°C); (b) free energy of formation ΔG_i° 36.2 kcal mole^{-1}; (c) specific heat capacity C_p° = 46.8 cal deg^{-1} mole^{-1}; (d) entropy of vaporisation ΔS_e = 22.6 e.u.

Table 1. Physicochemical properties of the covalent tetrahydroborates.

Compound	M.p., °C	B.p., °C	Coefficients A and B in the equation $\lg P = A - B/T$	ΔH_f (1) ΔH_e^f (2)	ΔH_{rev}	Density, g cm^{-3}
$Al(BH_4)_3$	−64.5[28]	44.5[28]	A B 7.808 1565[35] 9.56796 1799.1[36]	1.68[27] (1) 7.2 (2)	−72.1[37] −26.4[38] −74.7[7]	0.544 (20°)[28] 0.7866— 0.0007937[36]
$Be(BH_4)_2$		91.3 sublimation temp. (Ref.29)	11.772 3240[29]	14.81 (2)[29]	−25.8[7]	9.604 (20°)[7]
$U(BH_4)_4$	decompn. temp. >70[22]	—	13.65 4265[22]	—	—	—
$Zr(BH_4)_4$	29.7[24]	123 extrapolated	10.919 2983[24]	4 (1) 9.3 (2)[25]	—	1.13 (20°) 1.01 (30°)[39]
$Hf(BH_4)_4$	29[24]	118[24]	10.719 2983[24]	3 (1) 9.7 (2)[24]		1.85 (20°) 1.60 (30°)[39]
$Th(BH_4)_4$[24]	203 with decomposition	—	P=0.05 mmHg at 130° P=0.20 mmHg at 150°	—	—	—

As Table 1 shows, there has not yet been any serious investigation of the thermodynamic characteristics of covalent tetrahydroborates except for the melting and boiling points. For example, several values have been given for the heats of formation of aluminium tetrahydroborate, the reliability of these being equally doubtful. The difficulties in the determination of the thermodynamic characteristics of covalent tetrahydroborates are connected with their extremely high reactivity. For aluminium tetrahydroborate, for example, it is almost impossible to select an oxidant with which this compound will not react explosively during simple mixing under normal conditions.

Beryllium, aluminium, zirconium, hafnium, and uranium tetrahydroborates are less stable thermally than saltlike tetrahydroborates of univalent cations. Aluminium tetrahydroborate decomposes even at room temperature, with the formation of hydrogen. The decomposition is faster in the gas phase than in the liquid. Certain substances, for example, alloys of aluminium and copper, catalyse the decomposition[40]. Solutions of aluminium tetrahydroborate in saturated hydrocarbons with up to 50% $Al(BH_4)_3$ decompose at the same rate as the pure substance[41].

According to Schlesinger[11,42], aluminium tetrahydroborate is stabilised during prolonged storage under normal conditions or when heated for several days at 40°C. It is suggested that the stabilisation is linked with the formation of decomposition products which are inhibitors of further decomposition reactions.

The NMR spectrum of aluminium tetrahydroborate that has been kept for some time at 80°C differs from the spectra of "ordinary" aluminium tetrahydroborate[43]. The artificial introduction of diborane reduced the difference in the spectra, which suggested a reversible change by the following mechanism:

$$2\,Al(BH_4)_3 \rightleftarrows Al_2H_2(BH_4)_4 + B_2H_6\,. \qquad (13)$$

The probable mechanism of deuterium exchange between deuteriated diborane and aluminium tetrahydroborate[44] agrees with this assumption. However, the existence of $Al_2H_2(BH_4)_4$ in the gas phase is not confirmed by investigations of the infrared spectra[44].

Raising the temperature facilitates the more rapid decomposition of $Al(BH_4)_3$, with release of hydrogen and formation of a mixture of a crystalline powder and an amorphous black substance, which reacts with water with the release of hydrogen[45,46].

Beryllium tetrahydroborate is stable at room temperature and starts to decompose at 123°C.

The rate of decomposition of uranium and zirconium tetrahydroborates at room temperature is low; these substances are completely stable at 50—60°C. Further heating greatly increases the rate of pyrolysis. Uranium(IV) tetrahydroborate decomposes at 100°C with the formation of a red-brown uranium(III) tetrahydroborate[22]:

$$2\,U(BH_4)_4 \xrightarrow{100^\circ} 2\,U(BH_4)_3 + B_2H_6 = H_2\,. \qquad (14)$$

The decomposition of $U(BH_4)_4$ at 150°C leads to the formation of a metallic mirror on the walls of the pyrolyser and the release of hydrogen. Unlike uranium(IV) tetrahydroborate, uranium(III) tetrahydroborate is pyrophoric and decomposes explosively when heated. The decomposition of $U(BH_4)_4$ proceeds mainly in the gas phase and is accelerated in the presence of Hg, Cu, Ni, and "Pyrex" glass[22].

Zirconium and hafnium tetrahydroborates start to decompose at an appreciable rate when heated to 60—70°C.[24] Thorium tetrahydroborate decomposes slowly at 150°C and rapidly at 300°C. Its pyrolysis at 300°C leads to the formation of a metallic mirror of composition ThB_4, together with hydrogen[24].

The high reactivity of covalent tetrahydroborates in relation to oxygen and to compounds which contain positively polarised hydrogen atoms is due to the low strength of the MH_nB bridging bonds in the $M(BH_4)_n$ molecules, the unsaturated nature of these compounds, and their high heats of combustion or hydrolysis. Actually, all the covalent tetrahydroborates react with water even at ~—80°C.[47] The products of the reaction are the hydroxides of the corresponding metals, boric acid, and hydrogen. The hydrolysis of aluminium tetrahydroborate, like, probably, that of other tetrahydroborates, proceeds in stages, with the formation in the first stage of diborane, which is subsequently hydrolysed to hydrogen and boric acid[47,48]:

$$Al(BH_4)_3 + 3H_2O \rightarrow Al(OH)_3 + {}^3/_2B_2H_6 + 3H_2\,, \qquad (15)$$

$${}^3/_2B_2H_6 + 9H_2O \rightarrow B(OH)_3 + 9H_2\,. \qquad (16)$$

At room temperature aluminium and beryllium tetrahydroborates react explosively with water. However, in the hydrolysis only 70—80% of the theoretically necessary hydrogen is released and solid yellow—brown polymeric substances are formed[47].

The presence of traces of water (which is a catalyst of the oxidation) is necessary for the spontaneous ignition of mixtures of covalent tetrahydroborates and oxygen[24,29,50]. For example, uranium tetrahydroborate $U(BH_4)_4$ is only slowly oxidised in dry air, whereas all the covalent tetrahydroborates are spontaneously combustible in air[31,49-51].

The tetrahydroborates $M(BH_4)_n$ react with hydrogen chloride at −80°C with the formation of the chlorides of the corresponding metals, diborane, and hydrogen[24,28]. The main side-reaction here is the formation of halogen-substituted boron hydrides, for example:

$$B_2H_6 + HCl \rightarrow B_2H_5Cl + H_2\,. \qquad (17)$$

IV. STRUCTURE

The most effective method of studying the structure of the molecules of the volatile covalent tetrahydroborates $M(BH_4)_n$ was gas electron diffraction.

Bauer and Beach[52] made the first studies in this field. They found the $Al(BH_4)_3$ molecule to have the configuration of a trigonal prism with an equilateral triangle of B atoms in the equatorial plane. The Al atom is situated at the centre of the triangle and the H atoms of the AlH_2B bridging bonds at the vertices of the trigonal prism.

In principle, the electron diffraction results also do not contradict the other possible model (octahedral)[53,54], which differs from that considered above in the angle of slope of the plane of the AlH_2B bonds to the plane of the AlB_3 triangle: in the prismatic model this angle is 90°, in the octahedral 45°. The symmetry element σ_h is absent from the octahedral model. The choice between the two possible configurations was made on the basis of a detailed investigation of the infrared and Raman spectra of gaseous[55,56] and liquid[57] $Al(BH_4)_3$ and its isotope-substituted analogues $Al(^{11}BD_4)_3$, $Al(^{10}BH_4)_3$, and $Al(^{10}BD_4)_3$. As Table 2 shows, for the D_{3h} prismatic model of the $Al(BH_4)_3$ molecule there should be 13 absorption bands in the infrared spectrum and 5 polarised and 14 non-polarised bands in the Raman spectrum. For the D_3 octahedral model there should be 21 absorption bands in the infrared spectrum and 7 polarised and 14 non-polarised bands in the Raman spectrum. The experimental results agree better with the prismatic model (see Table 2).

Almeningen and coworkers[58] further refined the interatomic distances and valence angles in the prismatic model of $Al(BH_4)_3$. The model of the $Al(BH_4)_3$ molecule according to Almeningen is given in Fig. 1.

The NMR spectra of aluminium tetrahydroborate were investigated in 1955 [43] and in 1967.[59].

In the 1967 analysis of the NMR spectra of various specimens of $Al(BH_4)_3$ [59] the possibility of the molecular polymorphism of $Al(BH_4)_3$ was suggested, linked with the reversible conversion of the prismatic molecule into the octahedral, which hypothetically exists in the liquid phase or in benzene solution. This hypothesis is based on the fact that the structure of the NMR spectra characteristic for a BH_4 group with four equivalent protons appears for specimens of $Al(BH_4)_3$ which have undergone different preliminary treatments and are in different states of aggregation at different temperatures. However, our results[60] do not agree with hypothesis of the molecular polymorphism of aluminium tetrahydroborate.

We showed that the infrared spectra of crystalline $Al(BH_4)_3$ are almost constant in the temperature range from −75° to −90°C and identical with the infrared spectrum of the gas phase at room temperature. The frequencies of the vibrations of the terminal BH_2 group in the spectrum of $Al(BH_4)_3$ are close to those of the corresponding vibratio in the infrared spectrum of diborane[61]. There is an

intense absorption band at 602 cm^{-1} belonging to the stretching vibrations of the Al—B bond. The intense absorption band corresponding to the B—B vibration is at 794 cm^{-1} in the diborane spectrum[61]. To understand the nature of the chemical bond in the $Al(BH_4)_3$ molecule, just as in other covalent tetrahydroborates, the ideas developed earlier by Lipscomb and coworkers[62] for boron hydrides can be applied. The molecular structure of aluminium tetrahydroborate can be interpreted as follows. Two types of bond ($BH_{termina}$ and Al—B) are "normal" two-centre bonds, for the formation of which the boron and aluminium atoms use three sp^2 hybrid atomic orbitals.

Table 2. Activity of the normal vibrations in the infrared and Raman spectra for prismatic and octahedral models.

Activity	No. of normal vibrations	Symmetry type	No. of normal vibrations	Activity
Raman	5	$A_1' > A_1$	7	Raman
—	2	A_1''		
—	3	$A_2' > A_2$	7	IR
IR	4	A_2''		
Raman, IR	9	$E' > E$	14	Raman, IR
Raman	5	E''		

The fourth atomic orbital of the boron, supposedly p_z, perpendicular to the plane in which lie the B—H and B—Al σ bonds, interacts with two s atomic orbitals of hydrogen atoms and one of the three pd^2 hybrid atomic orbitals of the aluminium atom to form four-centre molecular orbitals occupied by two electrons.

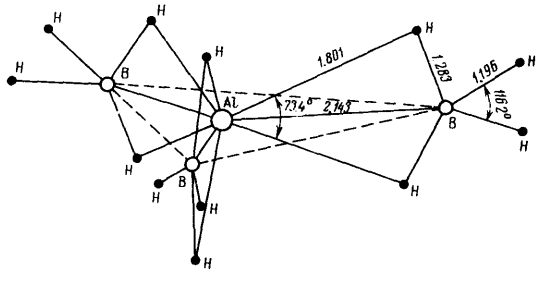


Figure 1. Model of the aluminium tetrahydroborate molecule.

Actually, the Al—B distance in the molecule is close to the sum of the so-called covalent radii and the BH_{bridge} and $Al—H_{bridge}$ distances are close to the corresponding distances in the B and Al hydrodes, in which these bonds are multicentre.

The crystal structure of aluminium tetrahydroborate was studied[60] in 1970. It forms two crystalline modifications (see Table 3) with enantiotropic transformation temperature of −76°C.

In the $Al(BH_4)_3$ crystal lattice all the intermolecular contacts are H---H contacts. The absence of any significant interaction between the molecules in the condensed phase explains the low melting point (−64.5°C) and boiling point (+44.5°C) of aluminium tetrahydroborate.

Table 3. Crystal-chemical results for the covalent tetrahydroborates.

Compound	Symmetry and unit-cell parameters				
	a, Å	b, Å	c, Å	space group	Z
α-Al $(BH_4)_3$	7.52	—	9.05	—	—
β-Al $(BH_4)_3$	7.50	12.15	5.94	$p2_12_12_1$	—
Be $(BH_4)_2$	13.59	—	9.92	$Fdcd$	16
Zr $(BH_4)_4$	5.86	—	—	$p\bar{4}3m$	1

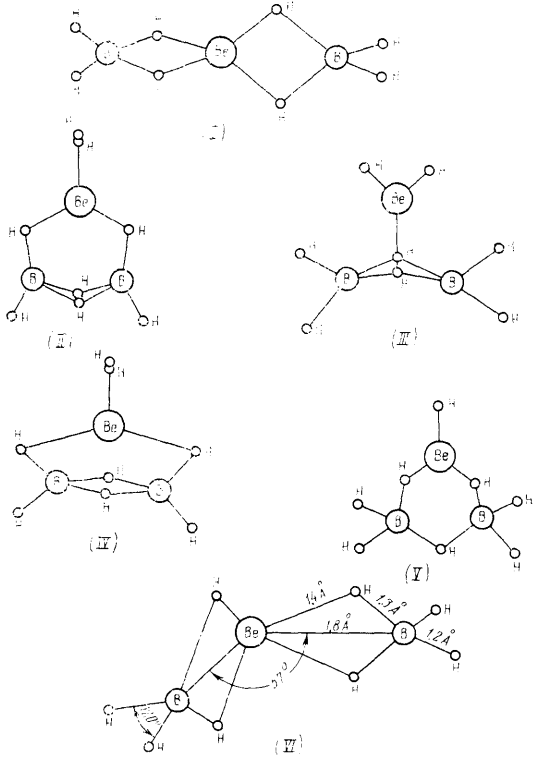


Figure 2. Molecular models of beryllium tetrahydroborate.

Silbiger and Bauer[54,63] were the first to investigate the molecular structure of beryllium tetrahydroborate $Be(BH_4)_3$ in the gas phase and they advanced two different interpretations of their experimental results. Both were based on the hypothesis of a linear configuration for the B—Be—B grouping. Fig. 2 (I) shows a model of the $Be(BH_4)_2$ molecule after Bauer[54]. Evidently, this model agrees well with classical views about the coordination four-covalency of beryllium.

In 1968 Almenningen and coworkers[1,64], in repeating the electron diffraction investigation of gaseous $Be(BH_4)_2$ by an improved experimental technique, came to an unexpected conclusion concerning the non-correspondence of Bauer's linear model with the experimental results. According to Almenningen, the three atoms (Be and B) are situated at the vertices of an almost regular triangle. The "triangular" configuration of the molecule agrees well with dipole moment (2.1 ± 0.5 D), measured[65] in 1969. Three polar molecular structures (Fig. 2, II, III, and IV) which exhibit the same symmetry C_{2v} can, in principle, be constructed on the base of the triangle of boron and beryllium atoms. Structures (II), (III), and (IV) are those of Almenningen, structure (V) was proposed by Cook[2] on the basis of a new interpretation (different from that of Almenningen and coworkers[1]) of the electron diffraction results.

Cook and Morgan[2] think that model (V) agrees better with the results of the investigation of the spectrum of beryllium tetrahydroborate, since it contains the $\diagdown BH_2$ grouping, which corresponds to the characteristic vibrations at 2630, 2531, and 974 cm^{-1} in the infrared spectrum†.

The presence of a band at 974 cm^{-1} is of special significance, since it has never before been observed in the infrared spectra of compounds with one terminal B—H bond[66].

In a further study of the infrared spectra of unsaturated vapour of $Be(BH_4)_2$ and its isotope-substituted analogues with ^{10}B and D, Cook and Morgan[67] were able to resolve P, Q, and R—the branches of the rotational structure in the spectrum. They showed the existence of terminal BH_2 groups and the absence of terminal BH groups in the $Be(BH_4)_2$ molecule.

An analysis of the vibrational-rotational contour of the absorption band with ν = 2521 cm^{-1} allowed the investigators to suggest the model of the $Be(BH_4)_2$ molecule shown in Fig. 2 (VI).

This model has C_{2v} symmetry. In the $\sigma_v(x, z)$ planes there are the boron atoms, the beryllium atom, and four terminal hydrogen atoms. The beryllium atom is linked with the boron atoms by twin hydrogen bridges. The planes of the bridging bonds are perpendicular to the $\sigma_v(x, z)$ plane.

The form of the infrared spectrum of saturated $Be(BH_4)_2$ vapour allowed the presence of polymeric beryllium tetrahydroborate molecules in this state to be proposed[67]. In 1952 Stosik[68] was the first to investigate the crystal structure of $Be(BH_4)_2$ (see Table 3), in 1952.

Marynick and Lipscomb[69] subsequently determined the dimensions and symmetry of the tetragonal unit cell more accurately (a = 13.62 ± 0.01 Å, c = 9.10 ± 0.01 Å, space group $I4\,Cd$) and interpreted the structure of beryllium tetrahydroborate in the crystalline phase.

In this structure the existence of polymeric spiral chains, not bonded to one another was observed. Polymerisation occurs owing to some of the BH_4 groups bonding beryllium atoms between them. The other BH_4 groups do not participate in the polymerisation and contain terminal BH_2 hydrogen bonds.

The structure of the zirconium tetrahydroborate $Zr(BH_4)_4$ molecule was investigated in both the crystalline and the gas phases by X-ray structural analysis and electron diffraction[70-72].

† The corresponding vibrations in the infrared spectrum of B_2H_6 are at 2612, 2525, 1035, and 979 cm^{-1}.

In every instance essentially the same result was obtained. The model of the $Zr(BH_4)_4$ molecule according to Plato and Heldberg's results[72] is shown in Fig. 3. Interestingly, in the $Zr(BH_4)_4$ molecule, unlike the $Al(BH_4)_3$ and $Be(BH_4)_2$ molecules, the $[BH_4]$ groups have C_{3v} symmetry and are connected with the zirconium atom by three hydrogen bridges. This symmetry of the BH_4 group and consequently of the molecular model with the metal atoms twelve-coordinated by hydrogen does not contradict the form of the infrared spectra of the zirconium and hafnium tetrahydroborates in the gas phase[73] and in solutions in non-polar solvents[73,74]. The intense absorption bands at 510 cm^{-1} and 602 cm^{-1} are assigned to the vibrations of the M—B bonds in zirconium and aluminium tetrahydroborates respectively. However, it is noteworthy that the spectrochemical investigations of these compounds are qualitative.

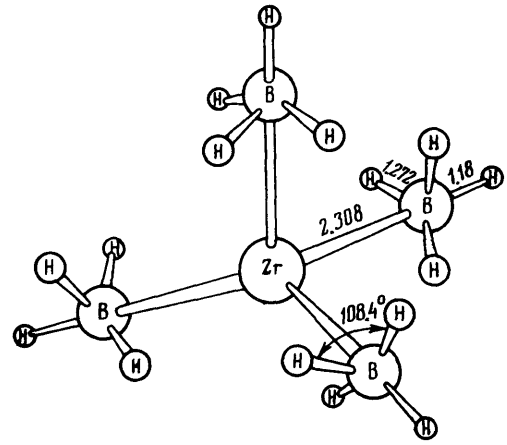


Figure 3. Model of the zirconium tetrahydroborate molecule.

The NMR spectrum of $Zr(BH_4)_4$ vapour[75] shows the equivalancy of all four protons in the BH_4 group. An analysis of the infrared spectrum of biscyclopentadienylzirconium bistetrahydroborate[76], that is, zirconium tetrahydroborate in which two BH_4 groups have been replaced by C_5H_5 groups, and an analysis of the infrared spectrum of $(C_5H_5)_2TiBH_4$ [77] showed the absence of absorption bands characteristic of BH_4^- ions in these compounds. The investigators suggested twin hydrogen bridging bonds between the boron atoms and the titanium and zirconium atoms. Consequently, unlike $Zr(BH_4)_4$, the local symmetry of the BH_4 group is C_{2v}. A comparison of the infrared spectra of these three compounds confirms the similarity of the infrared spectra of $(C_5H_5)_2Zr(BH_4)_2$ [76] and $TiBH_4(C_5H_5)_2$ and simultaneously the absence of the latter from the $Zr(BH_4)_4$ infrared spectra[73,74] in the range of the vibrations of the bridge and terminal B—H bonds, which shows that there are structural changes in the MBH_4 fragment in $(C_5H_5)_2Zr(BH_4)_2$ and $TiBH_4(C_5H_5)_2$ in comparison with $Zr(BH_4)_4$. The infrared spectra of the compounds $(Ph_3P_2)CuBH_4$,[78] $NiABH_4ClO_4$, and $NiA(BH_4)_2$ [79] (where A is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane) were interpreted on the basis of models with M—H—B and terminal BH_2 bonds.

In view of the fact that the structure of the $Be(BH_4)_2$ molecule in the vapour is still the subject of discussion some spectroscopic investigations have been made[80,81], which seemed desirable for an attempt at interpreting the infrared spectra of the unsaturated vapour of $Be(BH_4)_2$ itself.

A spectroscopic study of $MeBeBH_4$ vapour showed[81] that its gas phase is a mixture of monomeric and dimeric molecules. An analysis of the lines of the infrared spectrum allowed Cook and Morgan[81] to conclude that for both the monomeric and the dimeric molecules the skeleton was linear. The absorption bands in the $MeBeBH_4$ spectrum were assigned on the basis of the infrared spectrum of the Me_2Be vapour[80] and of the results obtained in the replacement of the boron and hydrogen atoms in the $MeBeBH_4$ molecule by the isotopes ^{11}B and D.

These results seemed useful in the assignment of the absorption bands in the spectrum of the $Be(BH_4)_2$ molecule in the vapour[67]. According to this assignment the absorption band with wavenumber 1014 cm^{-1} corresponds to the vibration of the Be—B bond and the absorption bands with wavenumbers 2172, 2069, and 1545 cm^{-1} to the vibrations of the BeH_2B fragment of the $Be(BH_4)_2$ molecule.

Since the experimental results on which the structural chemistry of the covalent tetrahydroborates is based are few and not systematic, it is at present impossible to draw a reliable picture of the nature of the chemical bond in the $M(BH_4)_n$ molecules.

However, undoubtedly the classical ideas of the valence and stereochemical possibilities of the atoms of the light metals Be and Al seem inapplicable for describing the structure and chemical properties of these compounds.

V. CHEMICAL REACTIONS

1. REACTION OF THE TETRAHYDROBORATES $M(BH_4)_n$ WITH ALKENES

Reactions of this type have been studied only for aluminium tetrahydroborate. Gaseous aluminium tetrahydroborate reacts readily at room temperature with ethylene, propene, and but-1-ene[82]. As a result of the reaction boron alkyls are formed, presumably with alkyl-substituted aluminium tetrahydroborates. Since the reaction rate is independent of the alkene concentration, the following possible mechanism is proposed for it:

$$Al(BH_4)_3 \rightleftarrows Al(BH_4)_2H + BH_3\,, \quad (18)$$

$$Al(BH_4)_2H + CH_2=CHR \rightarrow Al(BH_4)_2CH_2CH_2R\,, \quad (19)$$

$$BH_3 + 3\,CH_2=CHR \rightarrow B(CH_2CH_2R)_3\,. \quad (20)$$

The conversion rate is increased in the presence of traces of oxygen. The final products (boron alkyls) are inhibitors[82,83]. The reaction of aluminium tetrahydroborate with butadiene is more complex and evidently is not described by such a simple scheme[83].

2. REACTION WITH COMPOUNDS CONTAINING AN M—R BOND

Uranium tetrahydroborate reacts with trimethylboron at 50—60°C with the formation of methyldiborane and a green viscous liquid. Its fractionation allows us to obtain compounds of composition $U(BH_4)_3(CH_3BH_3)$ and $U(BH_3CH_3)_4$, which react with water, hydrogen chloride, and diborane, with the formation of methylboric acid or methyldichloroborane, uranium tetrahydroborate, and alkyl-substituted boranes[22]:

$$U(BH_3CH_3)_4 + 12\,HCl \rightarrow UCl_4 + 12H_2 + 4CH_3BCl_2\,, \quad (21)$$

$$U(BH_3CH_3)(BH_4)_3 + 12\,H_2O \rightarrow U(OH)_4 + 15\,H_2 + CH_3B(OH)_2 + 3HBO_2\,, \quad (22)$$

$$U(BH_3CH_3)(BH_4)_3 + B_2H_6 \rightarrow U(BH_4)_4 + CH_3BH_2BH_3\,, \quad (23)$$

$$U(BH_3CH_3)_4 + B_2H_6 \rightarrow U(BH_4)_4 + (CH_3)_4B_2H_2\,. \quad (24)$$

Reactions analogous to those described above, namely those leading to complication of the BH_4 group without change in the AlH_nB-bridging bonds are also known for aluminium tetrahydroborate, since its reaction with tetraborane and decaborane in ether lead to the formation of a series of compounds $Al(BH_4)_{3-x}(B_3H_8)_x$, where $x = 1$, 2, or 3, and $Al(BH_4)_{3-x}(B_{10}H_{13})_x$, where $x = 1$ and 2, respectively[84].

Aluminium tetrahydroborate[85] reacts vigorously with tetramethyltin and tetramethyl-lead with the formation of intermediate unidentified solid products, which decompose into Sn or Pb, H_2, methylated boranes, and $CH_3Al(BH_4)_2$. It is assumed that the intermediate unstable products have the composition $(CH_3)_2Sn(BH_4)_2$ and $(CH_3)_3Pb(BH_4)$. Aluminium tetrahydroborate reacts with trimethylchlorosilane according to the equation:

$$2\,Al(BH_4)_3 + 6\,(CH_3)_3SiCl \rightarrow 2AlCl_3 + 3B_2H_6 + 6\,(CH_3)_3SiH\,. \quad (25)$$

However, in silicon tetrachloride hydrogenation of the Si—Cl bonds by aluminium tetrahydroborate does not take place[86].

3. REACTION WITH OTHER ORGANIC COMPOUNDS

With organic and organosilicon compounds which are capable of being reduced the covalent tetrahydroborates react as very strong reductants. An example is the reaction of uranium tetrahydroborate with methyl borate[22]:

$$6\,U(BH_4)_4 + 2\,B(OCH_3)_3 \rightarrow 6\,U(BH_4)_3(BH_3OCH_3) + B_2H_6\,, \quad (26)$$

or that of aluminium tetrahydroborate with ethyl orthosilicate[85]:

$$2\,Al(BH_4)_3 + Si(OC_2H_5)_4 \rightarrow 2\,B_2H_6 + SiH_4 + 2Al(BH_4)\cdot(OC_2H_5)_2\,. \quad (27)$$

4. REACTION WITH NUCLEOPHILIC AGENTS—WITH NEUTRAL MOLECULES (L) OR IONS (X^-)

Reactions of this type are of the greatest interest. They are specific for the covalent tetrahydroborates and allow compounds of a new type to be obtained, containing Al and Be atoms in unusual valence states.

a. Formation of Compounds Containing the Anionic Complexes $[M(BH_4)_nX]^-$

The first mention of the formation of the complexes $M'X.M''H_n.mBH_3$, where M' is an alkali metal and M'' = Al or Be, was made in Wiberg's patents[87,88] in which the possibility of obtaining such compounds by the action of the corresponding covalent tetrahydroborate or of its ethereal solutions on the salts of alkali metals, or by the reaction of lithium tetrahydroaluminate with diborane in ethereal solutions was mentioned. In the latter instances, complexes containing the ether were formed.

Nöth[9], in referring to unpublished results[89], suggested the formation of such compounds in the reaction mixture in the production of aluminium tetrahydroborate by reaction (2).

Ashby and Foster[90] subsequently queried the existence of complexes in ethereal solutions. Later investigations of Nöth and coworkers[91] showed the possibility of the existence of equilibria in the $MX-Al(BH_4)_3-Et_2O$ systems:

$$Al(BH_4)_3 + LiX \xrightarrow{Et_2O} Li[Al(BH_4)_3X] \rightleftarrows LiBH_4 + Al(BH_4)_2X . \quad (28)$$

Complexes stable at room temperature were also obtained containing large organic or inorganic cations $[N(C_2H_5)_4][Al(BH_4)]_4$,[92] $[(C_8H_{17})_3NC_3H_7][Al(BH_4)_4]$, $[(C_8H_{17})_3NC_3H_7][Be(BH_4)_3]$, $[(C_8H_{17})_3NC_3H_7]_2[Be(BH_4)_5]$,[93] $[(C_4H_9)_4N][Al(BH_4)_4]$,[94] $K[Al(BH_4)_3Cl]$, and $K[Al(BH_4)_4]$.[95]

The stability of complexes with complex anions is known to depend on the charge : radius ratio of the outer-sphere cation z/r. For example, in the series $LiAlH_4-KAlH_4$ or $LiBH_4-KBH_4$ the thermal stability of the compounds increases rapidly. There is a similar regularity in the present instance. Actually, when the vapour pressure of aluminium tetrahydroborate above the complex $Li[Al(BH_4)_4]$ [88] is 2 mmHg the complexes with large organic cations, for example, $[N(C_2H_5)_4][Al(BH_4)_4]$ do not dissociate into the initial products even at 140°C.[92,94] The compounds $K[Al(BH_4)_3Cl]$ and $K[Al(BH_4)_4]$ probably have a somewhat lower stability and disproportionate at 130°C with an appreciable endothermic effect. It is noteworthy that the decomposition of the complexes at this temperature differ; whereas the complex $K[Al(BH_4)_4]$ dissociates mainly into the initial KBH_4 and $Al(BH_4)_3$, the compound $K[Al(BH_4)_3Cl]$ decomposes according to the following probable mechanism:

$$K[Al(BH_4)_3Cl] \rightarrow Al(BH_4)_2Cl + KBH_4 , \quad (29)$$

$$Al(BH_4)_2Cl \rightarrow \begin{cases} Al(BH_4)_3 + AlCl_3 \\ AlB_xH_yCl + B_2H_6 + H_2 . \end{cases} \quad (30)$$

The NMR spectrum of solutions of the complexes $[(C_8H_{17})_3NC_3H_7][M(BH_4)_n]$ suggests the equivalence of all the BH_4 groups in the $[M(BH_4)_n]^{m-}$ anion[93].

b. Reaction with the Formation of Molecular Compounds of the $M(BH_4)_n.mL$ Type

Oxonium and sulphonium complexes. Beryllium and aluminium tetrahydroborates dissolve in ethers with considerable evolution of heat and with the formation of complexes, the composition and properties of which are given in Table 4.

The reactivity of the oxonium complexes and of their solutions is less than that of the initial tetrahydroborates—in air, they are oxidised and hydrolysed slowly, without spontaneous combustion; it reacts violently with water, but without explosion. At room temperature in a dry atmosphere the oxonium complexes are relatively stable and decompose at an appreciable rate only at 40—50°C.

Desolvation of the oxonium complexes is accompanied by decomposition of the molecules of the tetrahydroborate and ligand[34].

It is known that the equilibrium in the system:

$$Al(BH_4)_3Me_2S + Me_2O \rightleftarrows Al(BH_4)_3Me_2O + Me_2S \quad (31)$$

is shifted almost entirely to the side of the formation of $Al(BH_4)_3Me_2O$, which shows that the strength of the oxonium Al←O bond is greater than that of the sulphonium Al←S bond.

In several instances the interaction of tetrahydroborates with liquid and solid ligands is identical. For example, beryllium tetrahydroborate reacts with THF vapour at room temperature to form the saltlike complex $Be(C_4H_8O)_4(BH_4)_2$,[27] in the infrared spectrum of which absorption bands characteristic for the isolated BH_4^- group are present. In the reaction of the same compounds in the liquid phase a vitreous substance of indefinite composition is formed[27]. This is probably brought about by irreversible interaction of the complex formed initially with the excess of ligand. The corresponding complex of aluminium tetrahydroborate reacts with the excess of THF with loss of a BH_3 group[34], evidently in the form $BH_3.C_4H_8O$.

Table 4. Some physicochemical properties of oxonium complexes of beryllium, aluminium, and zirconium tetrahydroborates.

Compound	M.p., °C	p_{sat}, mmHg
$Be(BH_4)_2 \cdot Et_2O$	liquid at 20°C	—
$Be(BH_4)_2 \cdot 4C_4H_8O$	solid at 20°C	—
$Al(BH_4)_3 \cdot Me_2O$	0—1	0.5 at 20°C
$Al(BH_4)_3 \cdot Et_2O$	0.5—1.5	7.8 at 85°C
$Al(BH_4)_3 \cdot C_4H_8O$	24—26	—
$2[Be(BH_4)_2] \cdot 3[C_2H_4(OMe)_2]$	solid at 20°C	—
$Zr(BH_4)_4 \cdot C_4H_8O$	2	—

Oxonium complexes can also be obtained by other methods, for example, by reaction (12), which allows compounds of different composition described by the formula $H_nAl(BH_4)_{3-n}.xEt_2O$, where $x = 1$ or 2, to be obtained from the same initial substances taken in equal ratios. The second molecule of the ether in such complexes is weakly bound with the $H_nAl(BH_4)_{3-n}$ molecule and is readily removed in a vacuum. At elevated temperatures the decomposition of the complex proceeds further[34]. The diethyl ether in the compounds $H_nAl(BH_4)_{3-n}.xEt_2O$ is readily replaced by an equimolecular amount of THF:

$$H_nAl(BH_4)_{3-n} \cdot xEt_2O + xC_4H_8O \rightarrow H_nAl(BH_4)_{3-n} \cdot xC_4H_8O + xEt_2O \quad (32)$$

The thermal decomposition of the compound $HAl(BH_4)_2.2C_4H_8O$ was studied and takes place with the formation of butoxyaluminium bistetrahydroborate:

$$2HAl(BH_4)_2 \cdot 2C_4H_8O \rightarrow 2C_4H_8O + (BH_4)_2Al\langle \begin{matrix} O-C_4H_9 \\ O \end{matrix} \rangle Al(BH_4)_2 . \quad (33)$$

In addition to complexes with ethers, aluminium tetrahydroborate forms stable compounds of the $Al(BH_4)_3 \cdot Al(OR)_3$ type on reacting with the corresponding alkoxides. The complexes obtained are liquids or solids, which vaporise without decomposition in a high vacuum[96].

Systems which contain ethers and heavy metal tetrahydroborates have been studied insufficiently. It is only known that when Zr tetrahydroborate reacts with THF the compound $Zr(BH_4)_4.C_4H_8O$ is formed[96].

The existence of this compound was found on the basis of a study of the equilibrium diagram in the $Zr(BH_4)_4-C_4H_8O$ system. Interestingly, on the equilibrium diagrams

of the $Zr(BH_4)_4$—dioxan[98], $Zr(BH_4)_4$—n-C_6H_{14}, $Zr(BH_4)_4$—cyclo-C_6H_{12}, $Zr(BH_4)_4$—C_6H_6, and $Zr(BH_4)_4$—$C_6H_6Zr(BH_4)_4$—$C_6H_5CH_3$ [99] systems there are only simple eutectics. It is noteworthy that neither structural nor physicochemical investigations of the oxonium complexes of the tetrahydroborates of aluminium, beryllium, and the Group metals have yet been made.

Compounds with Ammonia. The reaction of covalent tetrahydroborates with ammonia has been studied only for aluminium tetrahydroborate. In various investigations[3,5,28,100,101] the existence of several compounds has been found: $Al(BH_4)_3.nNH_3$, where n = 1, 2, 4, and 6. The aluminium tetrahydroborate ammines are solid substances stable at room temperature. The first to be obtained was aluminium tetrahydroborate monoammine, by the reaction of $Al(BH_4)_3$ with ammonia, taken in equimolecular proportions, initially at −80°C and then at room temperature. An attempt by Bird and Wallbridge[5] to prepare the monoammine in toluene solution at 1 : 1 molar ratio of the reagents and −78°C led to the production of aluminium tetrahydroborate diammine. A solution of the hexa-ammine complex is formed in the reaction of aluminium tetrahydroborate with an excess of liquid ammonia.

Another method for making an ammoniacal solution of the hexammine complex is the electrolysis of alkaline tetrahydroborates in liquid ammonia:

$$3\,NaBH_4 + Al + 6NH_3 \rightarrow Al(BH_4)_3 \cdot 6\,NH_3 + 3\,Na\,. \qquad (34)$$

A dissolving anode served as a source of aluminium[102]. When ammonia was removed from the solution, aluminium tetrahydroborate hexammine, stable at room temperature, was precipitated; it evidently contained clathrate ammonia[3]. X-Ray diffraction analysis showed the crystal structure of only a clathrate of composition $Al(BH_4)_3.6.7NH_3$.[3,5,99,101]. The infrared and NMR spectra show the presence of BH_4^- ions in the hexammine[5]. The ammoniacal solutions of aluminium tetrahydroborate hexammine evidently contain these ions, which react with aluminium chloride to form aluminium chloride hexammine and hydrogen:

$$Al(BH_4)_3(NH_3)_6 + 6\,NH_4Cl \rightarrow AlCl_3(NH_3)_6 + 3\left[\begin{matrix}NH_3\\NH_3\end{matrix}\!\!>\!BH_2\right]Cl + 6H_2\,. \qquad (35)$$

The reaction of aluminium tetrahydroborate hexammine with lithium in ammonia at −40°C proceeds according to the equation:

$$Al(NH_3)_6(BH_4)_3 + 2Li \rightarrow Li[Al(NH_2)_2(BH_4)_2] + H_2 + LiBH_4 + 4NH_3\,. \qquad (36)$$

The composition of the compound $Li[Al(NH_2)_2(BH_4)_2]$ was found by chemical analysis. Bird and Wallbridge[5] postulated the possibility of the $Al(H_2N)_2^+$ grouping in the anion of this complex being isoelectronic with allene $CH_2{=}C{=}CH_2$ and examined the possibility of its stabilisation according to the scheme $[H_2N{=}Al{=}NH_2]^+$.

Unlike aluminium tetrahydroborate its hexammine is slowly hydrolysed by cold water and is stable when heated to 50°C. When it is kept for a long period (11 days) at 50°C in a vacuum (10^{-5} mmHg) it yields a solid residue stable up to 400°C and the release of ammonia and volatile boron-containing compounds. Heating for 8 h at 105°C leads to the formation of analogous products[100].

Evidently, saltlike aluminium tetrahydroborate hexammine is the final product of the reaction between $Al(BH_4)_3$ and ammonia. Heterolytic breaking of the AlH_2B bridging bonds, which occurs in the $Al(BH_4)_3$ molecule under the action of NH_3, is analogous to the formation of the so-called "diborane ammine":

$$\begin{matrix}H\\ \diagdown\\ Al\\ \diagup\\ H\end{matrix}\!\!>\!BH_2 + NH_3 \rightarrow \left[\begin{matrix}\\ \diagdown\\ Al:NH_3\\ \diagup\\ \\ \end{matrix}\right]^+[BH_4]^- \qquad (37)$$

$$\begin{matrix}H\\ \diagdown\\ B\\ \diagup\\ H\end{matrix}\!\!>\!BH_2 + NH_3 \rightarrow \left[\begin{matrix}\\ \diagdown\\ B:NH_3\\ \diagup\\ \\ \end{matrix}\right]^+[BH_4]^- \qquad (38)$$

It seems that the initial stage of this process is the formation of unstable non-saltlike addition products of the $Al(BH_4)_3.nNH_3$ type; these may include the monoammine and diammine described earlier[4,28].

Compounds with primary and secondary amines, phosphines, and hydrazine. Nothing has been published on the reaction of aluminium tetrahydroborate with primary and secondary amines, phosphines, and hydrazine. Beryllium tetrahydroborate forms the following complexes with these ligands: $Be(BH_4)_2.NH(CH_3)_2$; $Be(BH_4)_2.3NH(CH_3)_3$; $Be(BH_4)_2.PH(CH_3)_2$; $Be(BH_4)_2.4NH_2.(C_4H_9)$;[102-103] $Be(BH_4)_2.3N_2H_4$.[104]

The monodimethylamine and phosphine derivatives are liquids; the others are crystalline[103-105]. It is suggested that like $Be(BH_4)_2.4C_4H_8O$ the complex of monobutylamine with beryllium tetrahydroborate has a saltlike structure with a BH_4^- anion[103].

The melting point has been measured only for tris(dimethylamine)beryllium tetrahydroborate (94°C), which decomposes at that temperature with release of hydrogen and the amine.

Compounds with tertiary amines, phosphines, and trimethylarsine. 1:1 complexes of beryllium and aluminium tetrahydroborates with tertiary amines or phosphines are obtained at low temperatures in the absence of an excess of the ligand. It is convenient to carry out the reaction in the presence of an inert solvent[104,106].

Table 5. Physicochemical properties of complexes of composition $M(NH_4)_nL$.

Compound	M.p., °C	T_{decomp}, °C	Other properties
$Be(BH_4)_2 \cdot N(CH_3)_3$	35	~140	$\lg P_{mmHg} = 8.353 - 2909/T$
$Al(BH_4)_3 \cdot N(CH_3)_3$	79 in rapid heating	50	monomer in vapour monomer in C_6H_6
$Al(BH_4)_3 \cdot N(C_2H_5)_3$	solid at 25°C	50	monomer in C_6H_6
$Be(BH_4)_2 \cdot P(CH_3)_3$	liquid at 20°C	--	volatile in a vacuum
$Be(BH_4)_2 \cdot P(C_2H_5)_3$	liquid at 20°C	—	P_{mmHg} = 0.01 at 68°C
$Be(BH_4)_2 \cdot PPh_3$	163 (decomp.)	122	monomer in C_6H_6
$Al(BH_4)_3 \cdot P(CH_3)_3$	78	—	monomer in C_6H_6
$Al(BH_4)_3 \cdot PPh_3$	186 (decomp.)	>70	monomer in C_6H_6
$Al(BH_4)_3 \cdot As(CH_3)_3$	57	—	—

Compounds of composition $M(BH_4)_n.L$ have been studied in relative detail. The physicochemical properties of such complexes are in Table 5.

As Table 5 shows, the 1 : 1 compounds are stable under ordinary conditions. The decomposition temperatures of most of the compounds have been determined but their pyrolysis has been insufficiently studied. An analysis of

published papers suggests that during the pyrolysis trialkylaminoboranes or trialkylphosphineboranes are formed, which are evidently thermodynamically the most stable compounds in the "ternary systems" MH_n—B_2H_6—NR_3 or MH_n—B_2H_6—PR_3.[4,28]

The amine and phosphine complexes of aluminium tetrahydroborate react with an excess of the ligand according to the following probable equation:

$$Al(BH_4)_3L \overset{+L}{\rightleftarrows} Al(BH_4)_3 \cdot 2L \rightleftarrows 'Al(BH_4)_2HL + BH_3L \overset{+L}{\rightleftarrows} \ldots\ldots \overset{+L}{\rightleftarrows} AlH_3 \cdot L\ddagger \quad (39)$$

Unlike the complexes of aluminium tetrahydroborate with tertiary amines and phosphines, the arsonium complex of composition $Al(BH_4)_3.As(CH_3)_3$ does not react with an excess of the ligand. The complex readily participates in an exchange reaction with trimethyl phosphine with the formation of $Al(BH_4)_3.P(CH_3)_3$, which is probably due to the greater strength of the Al←P bond compared with that of Al←As.

As already noted, beryllium tetrahydroborate does not form 1 : 2 complexes with trimethylamine and trimethylphosphine. When the trimethylamine complex of beryllium tetrahydroborate is heated it reacts with an excess of trimethylamine thus[29]:

$$Be(BH_4)_2 \cdot N(CH_3)_3 + N(CH_3)_3 \xrightarrow{100^\circ} \{HBe(BH_4)N(CH_3)_3\}_n + BH_3N(CH_3)_3 \quad (42)$$

The reaction of the phosphine complex of beryllium tetrahydroborate with an excess of the ligand evidently leads to the formation of beryllium hydride, which contains a certain amount of trialkylphosphine[102,103]:

$$Be(BH_4)_2 \cdot PR_3 + PR_3 \xrightarrow{70-180^\circ} \{BeH_2\}_n + 2PR_3BH_3 \quad (43)$$

The infrared spectra of compounds of aluminium tetrahydroborate and tetradeuterioborate with $N(CH_3)_3$, $P(CH_3)_3$, $As(CH_3)_3$, Et_2O, Me_2O, and Me_2S have been recorded[5,110] in the range 400—4000 cm^{-1}. Quantitative analysis and comparison of these spectra allows the following conclusions to be drawn:

1. Usually the frequencies of the vibrations in the coordinated $Al(BH_4)_3$ molecule are hardly displaced at all in comparison with the frequencies of the vibrations in free compounds.
2. Judging by the positions of the absorption bands characteristic for terminal BH_2 bonds, the structure of the tetrahydroborate group in the $Al(BH_4)_3.L$ molecules remains approximately the same as in the initial aluminium tetrahydroborate.
3. The equivalency of the three BH_4 groups in the $Al(BH_4)_3.L$ molecules can be postulated, since the significant splitting of the absorption bands belonging to the Al—H and B—H bridging vibrations was not observed.
4. The absorption bands due to the Al—B vibrations are shifted in the infrared spectra of the complexes into the longwave range, which can be interpreted as an increase in the Al—B interatomic distance, due to an expansion of the coordination sphere of the Al atom and an increase in its coordination number.

‡ The compounds $AlH_x(BH_4)_{3-x}L$, which are intermediates in reaction (39), were obtained independently by the reaction:

$$AlCl_{3-x}H_xN(CH_3)_3 + LiBH_4 \xrightarrow{C_6H_6} AlH_x(BH_4)_{3-x} \cdot N(CH_3)_3 + LiCl \quad (40)$$

Trialkylsiloxane derivatives of aluminium tetrahydroborate can be obtained in a similar manner:

$$R_3SiOAlCl_2 + 2LiBH_4 \xrightarrow{Et_2O} R_3SiOAl(BH_4)_2 + LiCl \quad (41)$$
$$(R = CH_3 \text{ or } C_2H_5)^{109}$$

However, these conclusions do not agree completely with the results of a direct X-ray diffraction investigation of the molecular structure of the complex $Al(BH_4)_3.N(CH_3)_3$.[111,112] Bird and Wallbridge observed two different molecular configurations of the complex $Al(BH_4)_3.N(CH_3)_3$. —"high-temperature" and "low temperature".

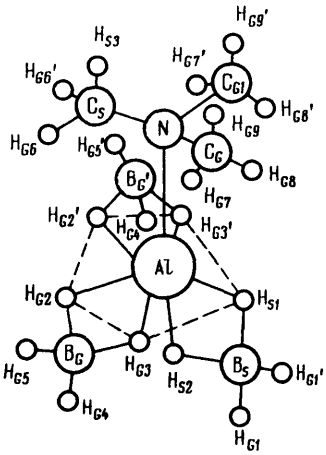


Figure 4. Model of a molecule of the compound $Al(BH_4)_3.N(CH_3)_3$.

In the "high-temperature" modification the B and N atoms are situated at the vertices of an almost regular tetrahedron, at the centre of which is the Al atom. The coordinates of the H atoms were not determined in this study, therefore the form and symmetry of the $[AlX_n]$ polyhedron, where X = N, B, or H cannot be determined.

Evidently, the investigations[5,11] of the infrared spectra relate to this configuration of the $Al(BH_4)_3.N(CH_3)_3$ molecule. An investigation of the low-temperature configuration at −160°C was more complete. The model of the $Al(BH_4)_3.N(CH_3)_3$ molecule is given in Fig. 4; Table 6 gives the valence angles and interatomic distances.

The boron atoms in the $Al(BH_4)_3.N(CH_3)_3$ molecule are clearly non-equivalent, the Al—H_{bridge} distances differing markedly from one another: from 1.75—1.83 Å for the Al—B_G group to 1.95—2.00 Å for the AlB_S group.

The coordination polyhedron around the aluminium atom is a distorted pentagonal bipyramid. Interestingly, whereas the Al—N interatomic distance is almost equal to the sum of the covalent radii of Al and N and does not differ from the Al—N interatomic distances in the molecules of the trialkylaminealanes $AlH_3.nNR_3$,[114] the Al—B interatomic distance is considerably greater than that in the $Al(BH_4)_3$ molecule, 2.257 Å compared with 2.14 Å.

An analysis of the structure suggests that it is produced by the displacement of one of the BH_4 groups, namely the group situated in the "trans position" to the $N(CH_3)_3$ molecule.

Actually, under the action of an excess of the ligand such a displacement takes place very readily, as already noted above . Evidently, in the $Al(BH_4)_3.N(CH_3)_3$ molecule and in the molecules (monotypical with it) of the complexes with trimethylphosphine, trimethylarsine,

triethylamine, etc., the atom for the formation of four two-centre bonds (three Al—B and one Al—L) uses a set of four sp^3 hybrid atomic orbitals.

Table 6. Valence angles and interatomic distances for the low-temperature configuration of $Al(BH_4)_3.N(CH_3)_3$.

$r_{Al-N} = 1.989 \pm 0.008$ Å	$B_S H_4$: $r_{B_S-H_{S1}} = 1.48 \pm 0.10$Å
$r_{Al-B_S} = 2.257 \pm 0.012$ Å	$r_{B_S-H_{S2}} = 1.16 \pm 0.011$Å
$r_{Al-B_G} = 2.227 \pm 0.011$Å	$r_{B_S-H_{G1}} = 1.15 \pm 0.08$Å
$r_{Al-H_{S1}} = 2.00 \pm 0.10$Å	$r_{H_{S1}-H_{S2}} = 2.29 \pm 0.15$Å
$r_{Al-H_{S2}} = 1.95 \pm 0.11$Å	$B_G H_4$: $r_{B_G-H_{G2}} = 1.18 \pm 0.07$Å
$r_{Al-H_{G2}} = 1.83 \pm 0.07$Å	$r_{B_G-H_{G3}} = 1.40 \pm 0.07$Å
$r_{Al-H_{G3}} = 1.75 \pm 0.08$Å	$r_{B_G-H_{G4}} = 1.22 \pm 0.11$Å
$\angle (N-AlH_{S2}) = 152.8 \pm 3.3°$	$r_{H_{G2}-H_{G3}} = 2.06 \pm 0.10$Å

The three four-centre AlH_2B bonds are formed from the *d* atomic orbital of the aluminium without participation of the *p* atomic orbital as in the $Al(BH_4)_3$ molecule. Because of this the strength of the bridging bonds in the $Al(BH_4)_3.L$ molecule should evidently be less than in the aluminium tetrahydroborate molecule. It is noteworthy that the existence of complexes of composition $Al(BH_4)_3.2L$ (see p. 10) does not contradict the above views.

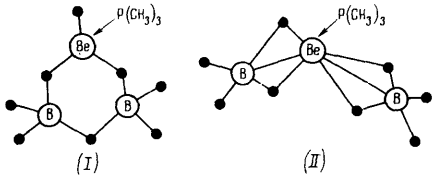


Figure 5. Probable structures of the $Be(BH_4)_2.P(CH_3)_3$ molecule.

The molecular structures of such compounds is of considerable interest. It can be postulated that the coordination polyhedron of the aluminium atom formed by the B and L atoms will be like that in the molecule of bistrimethylamine alane $AlH_3.2N(CH_3)_3$ with location of the boron atoms in the equatorial plane of the trigonal bipyramid.

X-Ray diffraction investigations of the complex derivatives of beryllium, zirconium, hafnium, thorium, and uranium tetrahydroborates have not yet been made.

A qualitative analysis of the infrared and NMR spectra of the compound $Be(BH_4)_2.P(CH_3)_3$ [103,104] allowed it to be ascribed the probable structure shown in Fig. 5 (I).

However, taking into account the most recent results on the structure of beryllium tetrahydroborate in the gas phase[68] another model of the structure of the $Be(BH_4)_2.PMe_3$, Fig. 5 (II), seems more probable.

It must be noted that the addition of a second molecule of the ligand to a beryllium tetrahydroborate molecule is always accompanied by the breaking of the Be—H—B bridging bonds. For example, the complexes $Be(BH_4)_2.4C_4H_8O$ and $Be(BH_4)_2.4C_4H_9NH_2$ are constructed from $[Be.4L]^{2+}$ cations and $[BH_4]^-$ anions[102].

This experimentally established fact can be explained as the consequence of the beryllium atom in the $Be(BH_4)_2L$ molecule using the entire set of four atomic orbitals and becoming "coordination saturated" as a result. It is to be hoped that further investigation of the structure and reactivity of the complexes of the tetrahydroborates of the light metals will yield results convenient for developing new ideas about the stereochemistry and nature of the chemical bond in the inorganic compounds of the light elements.

REFERENCES

1. A. Almenningen, G. Gundersen, and A. Haalaund, Acta chem. Scand., 22, 859 (1968).
2. T. H. Cook and G. L. Morgan, J. Amer. Chem. Soc., 91, 774 (1969).
3. J. C. Fauroux and S. J. Teichner, Bull. soc. chim. France, 4052 (1967).
4. P. H. Bird and M. G. H. Wallbridge, J. Chem. Soc. (A), 664 (1967).
5. P. H. Bird and M. G. H. Wallbridge, J. Chem. Soc. (A), 3923 (1965).
6. R. M. Adams and A. R. Sindle, "Boron, Met-Boron Compounds and Boranes", New York, 1964.
7. S. F. Sarner, "Propellant Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1969.
8. A. F. Zhigach and D. S. Stasinevich, "Khimiya Gidridov" (Chemistry of Hydrides), Izd. Khimiya, Leningrad, 1969.
9. H. Nöth, Angew. Chem., 73, 371 (1961).
10. J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium: The Element, Its Binary and Related Compounds" (Translated into Russian), Inostr. Lit., Moscow, 1956.
11. H. I. Schlesinger, H. C. Brown, and E. R. Hyde, J. Amer. Chem. Soc., 75, 209 (1953).
12. H. I. Schlesinger and H. C. Brown, US P. 2 599 203 (1952); Chem. Abs., 46, 221 601d (1952).
13. H. I. Schlesinger and H. C. Brown, J. Amer. Chem. Soc., 75, 203 (1953).
14. V. I. Mikheeva and S. Zapol'skii, Zhur. Neorg. Khim., 15, 633 (1970) [Russ. J. Inorg. Chem., No. 3 (1970)].
15. W. M. Olson and R. T. Sandersen, J. Inorg. Nuclear Chem., 7, 228 (1958).
16. W. Schechter, US P. 2 913 306 (1959); Ref. Zhur. Khim., 2K48 (1961).
17. J. B. Hinkamp and Y. Haizda, Ind. Eng. Chem., 47, 1560 (1955).
18. J. B. Hinkamp, US P. 2 657 975 (1953); Ref. Zhur. Khim., 7848P (1955).
19. J. B. Hinkamp, US P. 2 854 312 (1958); Ref. Zhur. Khim., 48 410P (1960).
20. J. C. Fauroux and S. J. Teichner, Bull. soc. chim. France, 3014 (1966).
21. W. E. Reid, J. M. Bish, and A. Brenner, J. Elektrochem. Soc., 104, 21 (1957).
22. H. I. Schlesinger and H. C. Brown, J. Amer. Chem. Soc., 75, 219 (1953).
23. H. I. Schlesinger and H. C. Brown, US P. 2 600 370 (1952); Chem. Abs., 46, P10 561a (1952).
24. H. R. Hoekstra and J. J. Katz, J. Amer. Chem. Soc., 71, 2488 (1949).
25. H. R. Hoekstra and J. J. Katz, US P. 2 575 750 (1951); Chem. Abs., 46, 2248e (1952).

26. M. D. Banus, R. W. Bragner, and A. A. Hinekly, J. Amer. Chem. Soc., 76, 3848 (1954).
27. H. I. Schlesinger, R. Sanderson, and A. Burg, J. Amer. Chem. Soc., 61, 536 (1939).
28. H. I. Schlesinger, R. T. Sanderson, and A. Burg, J. Amer. Chem. Soc., 62, 3425 (1940).
29. A. B. Burg and H. I. Schlesinger, J. Amer. Chem. Soc., 62, 3421 (1940).
30. C. D. Barbaros, C. Dillart, A. C. Finholt, K. E. Wilzbern, T. Wartik, and M. I. Schlesinger, J. Amer. Chem. Soc., 73, 4585 (1951).
31. A. E. Finholt, A. C. Bond, and H. I. Schlesinger, J. Amer. Chem. Soc., 69, 1199 (1947).
32. J. Kollonitsch and G. Fuchs, Nature, 17b, 181 (1955).
33. J. Kollonitsch and G. Fuchs, Hung. P. 143 422 (1957); Ref. Zhur. Khim., 35 015 (1960).
34. H. Nöth and H. Suchy, J. Organomet. Chem., 5, 197 (1966).
35. S. Smit and R. Miller, J. Amer. Chem. Soc., 72, 1452 (1950).
36a. E. C. Kerr, N. C. Hallet, and H. L. Johnston, Ohio State Univ., Tech. Rept. 10, Contr. 6 ONR-225, 1952.
37. R. M. Rullon and L. S. Hason, J. Amer. Chem. Soc., 73, 5491 (1951).
38. S. S. Wise, Chem. Abs., 67, 155 271 (1967).
39. V. V. Volkov and O. I. Papiro, Zhur. Neorg. Khim., 11, 1476 (1966) [Russ. J. Inorg. Chem., No. 6 (1966)].
40a. H. I. Schlesinger, Univ. Chicago, N. Contr. 1739—9820, Find Rept., 1944—1945.
41a. R. S. Brokaw, Princeton Univ., Techn. Memo PR-9, 1948.
42a. H. I. Schlesinger, see Ref. 40 above.
43. R. A. Ogg and J. D. Reu, Disc. Faraday Soc., No. 215, 238 (1955).
44. C. P. Maylbery and J. C. Larrabee, Inorg. Chem., 2, 855 (1963).
45a. R. S. Brokaw, Princeton Univ. Techn. Memo PR-126, 1949.
46. R. S. Brokaw and R. N. Pease, J. Amer. Chem. Soc., 74, 1590 (1952).
47a. H. I. Schlesinger, US Off. Nav. Res., 72—329 t. 03, Find Rept., 1952.
48. M. Kilpatrik, J. Boker, and C. Mikinney, J. Phys. Chem., 57, 385 (1953).
49. E. J. Badin, R. S. Hunter, and W. Pease, J. Amer. Chem. Soc., 71, 2950 (1942).
50. A. E. Fletcher, B. H. Foster, and D. M. Steight, Ind. Eng. Chem., 51, 1383 (1953).
R. S. Brokaw, E. J. Badin, and R. N. Pease, J. Amer. Chem. Soc., 72, 1793 (1950).
52. J. Y. Beach and S. H. Bauer, J. Amer. Chem. Soc., 62, 3440 (1940).
53. H. C. Longuet-Higgins, J. Chem. Soc., 139 (1946).
54. S. H. Bauer, J. Chem. Soc., 622 (1950).
55. W. C. Prise, H. C. Higgins, R. Rice, and T. F. Joung, J. Chem. Phys., 17, 217 (1949).
56. W. C. Prise, J. Chem. Phys., 17, 1044 (1949).
57. A. R. Emery and R. C. Teylor, Spectrochem. acta, 16, 1455 (1960).
58. A. Almenningen, G. Gundersen, and A. Haaland, Acta chem. Scand., 22, 328 (1968).
59. P. C. Maybury and J. E. Ahnell, Inorg. Chem., 6, 1286 (1967).
60. K. N. Semenenko, O. V. Kravchenko, and E. B. Lobkovskii, Zhur. Strukt. Khim., 13, 540 (1972).
61. W. L. Smit and J. M. Mills, J. Chem. Phys., 41, 1479 (1964).
62. W. N. Lipscomb, W. H. Eberhardt, and B. Crawford, Uspekhi Khim., 25, 1249 (1956) [Translated into Russian, possibly from J. Chem. Phys., 22, 989 (1954)].
63. J. Silbiger and S. H. Bauer, J. Amer. Chem. Soc., 68, 312 (1946).
64. A. Almenningen, G. Gundersen, and A. Haaland, Chem. Comm., 557 (1969).
65. J. W. Niler and J. McNabb, Chem. Comm., 134 (1969).
66. L. J. Bellamy, W. Gerrard, M. F. Lappert, and R. L. Williams, J. Chem. Soc., 2412 (1958).
67. T. H. Cook and G. L. Morgan, J. Amer. Chem. Soc., 92, 6493 (1970).
68. I. Stosik, Acta Cryst., 1, 151 (1952).
69. D. S. Marynick and W. N. Lipscomb, J. Amer. Chem. Soc., 93, 2322 (1971).
70. P. H. Bird and M. P. Churchill, Chem. Comm., 403 (1967).
71. V. P. Spiridonov and G. I. Mamaeva, Zhur. Strukt. Khim., 10, 133 (1969).
72. V. Plato and K. Heldberg, Inorg. Chem., 10, 590 (1971).
73. V. V. Volkov, E. V. Sobolev, Z. A. Grankina, and I. S. Kalinina, Zhur. Neorg. Khim., 13, 659 (1968) [Russ. J. Inorg. Chem., No. 3 (1968)].
74. V. V. Volkov, E. V. Sobolev, E. E. Zaev, and O. N. Shapiro, Zhur. Strukt. Khim., 8, 461 (1967).
75. B. D. Jams, R. K. Nada, and M. G. Wallbridge, J. Chem. Soc. (A), 183 (1966).
76. R. K. Nada and M. G. H. Wallbridge, Inorg. Chem., 3, 1798 (1964).
77. H. Nöth and R. Hartrimmer, Chem. Ber., 43, 2238 (1960).
78. J. M. Davidson, Chem. a. Ind., 2021 (1964).
79. N. F. Gurtis, J. Chem. Soc., 924 (1965).
80. R. A. Kovar and G. L. Morgan, Inorg. Chem., 8 1089 (1969).
81. T. H. Cook and G. L. Morgan, J. Amer. Chem. Soc., 92, 6487 (1970).
82. R. S. Brokaw and R. N. Peas, J. Amer. Chem. Soc., 72, 3234 (1950).
83. R. S. Brokaw and R. N. Peas, J. Amer. Chem. Soc., 72, 5263 (1950).
84. W. V. Hough, US P. 3 238 012 (1966); Ref. Zhur. Khim., 6L97P (1967).
85. A. R. Hollidey and W. Jeffers, J. Inorg. Nuclear Chem., 6, 134 (1958).
86. N. G. Goodsped and R. T. Sanderson, J. Inorg. Nuclear Chem., 2, 266 (1958).
87. E. Wiberg and H. Neumeier, B P. 840—572 (1958); Chem. Abs., 56, 4366e (1962).
88. E. Wiberg and H. Neumeier, German P. 1 080 527 (1960); Chem. Abs., 55, 21 504b (1961).
89. E. Wiberg and G. N. Schrauzer, Diss., Univ. München, 1956.
90. E. C. Ashby and W. E. Foster, J. Amer. Chem. Soc., 88, 3248 (1966).
91. M. Ehemann, H. Nöth, N, Davies, and M. G. H. Wallbridge, Chem. Comm., 862 (1968).
92. L. V. Titov, E. R. Eremin, L. Gavrilova, and V. Ya. Rossolovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 180 (1970).
93. H. Nöth and M. Ehemann, Chem. Comm., 685 (1967).
94. K. N. Semenenko, O. V. Kravchenko, S. P. Shilkin, and V. B. Polyakova, Dokl. Akad. Nauk SSSR, 201, 1372 (1971).
95. K. N. Semenenko and O. V. Kravchenko, Zhur. Neorg. Khim., 17, 2085 (1972) [Russ. J. Inorg. Chem., No. 8 (1972)].

96. J. Kollonitsch, Nature, 189, 1006 (1961).
97. V. V. Volkov, K. G. Myakishev, and G. I. Bagryantsev, Zhur. Neorg. Khim., 15, 1941 (1970) [Russ. J. Inorg. Chem., No. 7 (1970)].
98. V. V. Volkov, K. G. Myakishev, and G. I. Bagryantsev, Zhur. Neorg. Khim., 16, 233 (1971) [Russ. J. Inorg. Chem., No. 1 (1971)].
99. V. V. Volkov, K. G. Myakishev, and G. I. Bagryantsev, Izv. Sibir. Otdel. Akad. Nauk SSSR, Ser. Khim., B5, 145 (1969).
100. J. C. Fauroux and S. J. Teichner, Bull. soc. chim. France, 74 (1968).
101. R. Taylor, US Rept. Com., Off. Tech. Sew. Rapp. AD256 8873, 1961.
102. J. Plešěc, S. Nermanek, V. Gregor, and J. Vit, Czech. P. 0116101 (1965); Ref. Zhur. Khim., 21L163 (1967).
103. L. Banford and G. E. Coates, J. Chem. Soc., 5591 (1961).
104. L. Banford and G. E. Coates, J. Chem. Soc., 274 (1966).
105. L. Lamoria and P. F. Reigler, US P. 3346348 (1967); Ref. Zhur. Khim., 4L99 (1963).
106. P. H. Bird and M. G. H. Wallbridge, Chem. Comm., 291 (1965).
107. J. K. Ruff, Inorg. Chem., 2, 515 (1963).
108. J. K. Ruff, Adv. Chem. Soc., 42, 139 (1964).
109. B. Armer and H. Schmidbauer, Chem. Ber., 101, 2252 (1968).
110. N. Davies, P. H. Bird, and M. G. H. Wallbridge, J. Chem. Soc., 2269 (1968).
111. N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, Inorg. Chem., 7, 1575 (1968).
112. N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, Chem. Comm., 438 (1965).
113. N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, Chem. Comm., 286 (1966).
114. C. W. Heitsch, C. E. Nordman, and R. W. Parry, Inorg. Chem., 2, 508 (1963).

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a) Cited in the book: R. M. Adams and A. R. Sindle, "Boron, Metallo-Boron Compounds, and Boranes", Interscience, New York, 1964.

b) Cited by: H. Nöth, Angew. Chem., 73, 37 (1961).

c) Cited by: J. C. Fauroux and S. T. Teichner, Bull. soc. chim. France, 74 (1968).