Gmelin Handbuch der Anorganischen Chemie

Ergänzungswerk zur achten Auflage

New Supplement Series

Band 54

Borverbindungen

Teil 20

Bor-Wasserstoff-Verbindungen, Teil 3

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mit 113 Figuren

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DIE LITERATUR IST FÜR DIE REINEN BORWASSERSTOFFE VON 1950 BIS ENDE 1977, FÜR DIE DERIVATE BIS ENDE 1976 AUSGEWERTET

LITERATURE COVERAGE: 1950 THROUGH 1977 FOR THE BORON HYDRIDES, THROUGH 1976 FOR THE DERIVATIVES

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Preface

Boron hydrides containing five and more boron atoms in the molecule and those of their derivatives which were not previously discussed are the topic of the present volume "Borverbindungen" 20. This 54th volume of the New Supplement Series of the Gmelin Handbook concludes this particular presentation of boron compounds (see the listing on next pages). An index for all volumes of the New Supplement Series dealing with boron compounds is being prepared. Future supplements will be published as regular addition to the Main Series and will be arranged according to the Gmelin principle of the last position (see the illustration on the inside of the backcover).

The discussion of boron chemistry within the New Supplement Series provides a broadly concepted presentation of chemically related information. Thus, the material compiled in the 20 volumes extends far beyond the Gmelin principle of the last position. This event was significantly facilitated by the cooperation of external scientists, and their contributions are gratefully acknowledged.

Within the present volume the literature on pure boron hydrides is covered through 1977, that of the derivatives is covered through 1976.

Frankfurt am Main
Lexington, Kentucky (USA)
October 1979

Karl-Christian Buschbeck
Kurt Niedenzu

Boron and Boron Compounds in the Gmelin Handbook

"Bor" (Main Volume Syst.-No. 13)	Historical. Occurrence. The Element. Compounds of B with H, O, N, the Halogens, S, Se, and Te. Literature closing date: end of 1925.
"Bor" (Supplement Volume Syst.-No. 13)	Occurrence. The Element. Compounds of B with H, O, N, the Halogens, S, and C. Literature closing date: end of 1949.

New Supplement Series

"Borverbindungen" 1 (New Supplement Series Vol. 13)	Boron Nitride. B-N-C Heterocycles. Polymeric B-N Compounds. Literature coverage from 1950 up to 1972.
"Borverbindungen" 2 (New Supplement Series Vol. 15)	Carboranes, Part 1. Nomenclature and Types of Carboranes. Carboranes (without Hetero- and Metallocarboranes, and Higher Carboranes). Literature coverage from 1950 up to 1973 or 1970, respectively).
"Borverbindungen" 3 (New Supplement Series Vol. 19)	Compounds of B Containing Bonds to S, Se, Te, P, As, Sb, Si, and Metals. Literature coverage from 1950 to the end of 1973.
"Borverbindungen" 4 (New Supplement Series Vol. 22)	Compounds with Isolated Trigonal Boron Atoms and Covalent Boron-Nitrogen Bonding (Aminoboranes and B-N Heterocycles). Literature coverage from 1950 to the end of 1973.
"Borverbindungen" 5 (New Supplement Series Vol. 23)	Boron-Pyrazole Derivatives and Spectroscopic Studies on Trigonal B-N Compounds. Literature coverage from 1950 to the end of 1973.
"Borverbindungen" 6 (New Supplement Series Vol. 27)	Carboranes, Part 2. Hetero- and Metallocarboranes. Polymeric Carborane Derivatives. Electronic Properties. Literature coverage from 1950 up to 1974 or 1971, respectively.
"Borverbindungen" 7 (New Supplement Series Vol. 28)	Boron Oxides. Boric Acids. Borates. Literature coverage from 1950 to the end of 1973.
"Borverbindungen" 8 (New Supplement Series Vol. 33)	The Tetrahydroborate Ion and Its Derivatives. Literature coverage from 1950 to the end of 1974.
"Borverbindungen" 9 (New Supplement Series Vol. 34)	Boron-Halogen Compounds, Part 1. Literature coverage from 1950 to the end of 1974.
"Borverbindungen" 10 (New Supplement Series Vol. 37)	Boron Compounds with Coordination Number 4. Literature coverage from 1950 to the end of 1975.

"Borverbindungen" 11 (New Supplement Series Vol. 42)	Carboranes, Part 3. Dicarba-*closo*-dodecaboranes. Literature coverage from 1950 to the end of 1975.
"Borverbindungen" 12 (New Supplement Series Vol. 43)	Carboranes, Part 4. Dicarba-*closo*-dodecaboranes. Literature coverage from 1950 to the end of 1975.
"Borverbindungen" 13 (New Supplement Series Vol. 44)	Boron-Oxygen Compounds, Part 1. Literature coverage from 1950 to the end of 1975.
"Borverbindungen" 14 (New Supplement Series Vol. 45)	Boron-Hydrogen Compounds, Part 1. Literature coverage from 1950 to the end of 1975.
"Borverbindungen" 15 (New Supplement Series Vol. 46)	Amine-boranes. Literature coverage from 1950 to the end of 1975.
"Borverbindungen" 16 (New Supplement Series Vol. 48)	Boron-Oxygen Compounds, Part 2. Literature coverage from 1950 to the end of 1975.
"Borverbindungen" 17 (New Supplement Series Vol. 51)	Borazine and Its Derivatives. Literature coverage from 1950 to the end of 1976.
"Borverbindungen" 18 (New Supplement Series Vol. 52)	Boron-Hydrogen Compounds, Part 2. Literature coverage from 1950 to the end of 1976.
"Borverbindungen" 19 (New Supplement Series Vol. 53)	Boron-Halogen Compounds, Part 2. Literature coverage from 1950 to the end of 1976.
"Borverbindungen" 20 (New Supplement Series Vol. 54)	Boron-Hydrogen Compounds, Part 3. Literature coverage from 1950 to the end of 1976.

A systematic sequence of the individual chapters and an index for all volumes will complete the works.

Vorwort

Borwasserstoffe mit fünf und mehr Boratomen im Molekül sowie deren Derivate, soweit letztere nicht schon in früheren Bänden besprochen sind, sind das Thema des vorliegenden Bandes „Borverbindungen" 20. Mit diesem 54. Band des Ergänzungswerks zur 8. Auflage des Gmelin Handbuchs wird die Bearbeitung der Borverbindungen im Rahmen des Ergänzungswerks abgeschlossen. Als zusätzlicher Band erscheint noch ein Register für sämtliche Bände der Reihe „Borverbindungen" (s. die Aufstellung auf den nächsten beiden Seiten). Künftige Nachträge werden ausschließlich in Ergänzungsbänden zum Hauptwerk erscheinen, geordnet nach dem Gmelin-Prinzip der letzten Stelle (s. die Zusammenstellung auf der Innenseite des hinteren Einbanddeckels).

Bei der Behandlung der Borverbindungen im Ergänzungswerk wurden in vielen Fällen die Begrenzungen des Themas weit gefaßt, um dem Interesse des Benutzers an chemisch zusammenhängender Information entgegenzukommen. Die 20 den Borverbindungen gewidmeten Bände bieten eine weit über das Gmelin-Prinzip der letzten Stelle hinausgehende Zusammenstellung der Borchemie, die entscheidend durch die Mitwirkung auswärtiger Wissenschaftler ermöglicht wurde. Ihnen sei an dieser Stelle für ihre Tätigkeit gedankt.

Im vorliegenden Band ist die Literatur der reinen Borwasserstoffe bis Ende 1977, die der Derivate bis Ende 1976 berücksichtigt, in einigen Fällen auch darüber hinaus.

Frankfurt am Main
Lexington, Kentucky (USA)
Oktober 1979

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Kurt Niedenzu

Bor und Borverbindungen im Gmelin Handbuch

„Bor" (Hauptband Syst.-Nr. 13)	Geschichtliches. Vorkommen. Das Element. Verbindungen von B mit H, O, N, den Halogenen, S, Se und Te. Literaturschluß: Ende 1925.
„Bor" (Ergänzungsband Syst.-Nr. 13)	Vorkommen. Das Element. Verbindungen von B mit H, O, N, den Halogenen, S und C. Literaturschluß: Ende 1949.

Bände des Ergänzungswerks

„Borverbindungen" 1 (Erg.-Werk Bd. 13)	Bornitrid. B-N-C-Heterocyclen. Polymere B-N-Verbindungen. Literatur ab 1950. Literaturschluß: 1972.
„Borverbindungen" 2 (Erg.-Werk Bd. 15)	Carborane, Teil 1. Nomenklatur und Typen der Carborane. Carborane (ohne Hetero- und Metallcarborane sowie höhere Carborane). Literatur ab 1950. Literaturschluß: 1973 bzw. Ende 1970.
„Borverbindungen" 3 (Erg.-Werk Bd. 19)	Verbindungen mit S, Se, Te, P, As, Sb, Si und mit Metallen. Literatur ab 1950. Literaturschluß: Ende 1973.
„Borverbindungen" 4 (Erg.-Werk Bd. 22)	Verbindungen mit isoliertem trigonalen Boratom und kovalenter Bor-Stickstoff-Bindung (Aminoborane und B-N-Heterocyclen). Literatur ab 1950. Literaturschluß: Ende 1973.
„Borverbindungen" 5 (Erg.-Werk Bd. 23)	Bor-Pyrazol-Derivate und Spektroskopie trigonaler B-N-Verbindungen. Literatur ab 1950. Literaturschluß: Ende 1973.
„Borverbindungen" 6 (Erg.-Werk Bd. 27)	Carborane, Teil 2. Hetero- und Metallcarborane. Polymere Carboranverbindungen. Elektronische Eigenschaften. Literatur ab 1950. Literaturschluß: 1974 bzw. 1971.
„Borverbindungen" 7 (Erg.-Werk Bd. 28)	Boroxide. Borsäuren. Borate. Literatur ab 1950. Literaturschluß: Ende 1973.
„Borverbindungen" 8 (Erg.-Werk Bd. 33)	Das Tetrahydroborat-Ion und Derivate. Literatur ab 1950. Literaturschluß: Ende 1974.
„Borverbindungen" 9 (Erg.-Werk Bd. 34)	Bor-Halogen-Verbindungen, Teil 1. Literatur ab 1950. Literaturschluß: Ende 1974.
„Borverbindungen" 10 (Erg.-Werk Bd. 37)	Verbindungen mit vierfach koordiniertem Bor. Literatur ab 1950. Literaturschluß: Ende 1975.
„Borverbindungen" 11 (Erg.-Werk Bd. 42)	Carborane, Teil 3. Dicarba-*closo*-dodecaborane. Literatur ab 1950. Literaturschluß: Ende 1975.

„Borverbindungen" 12 (Erg.-Werk Bd. 43)	Carborane, Teil 4. Dicarba-*closo*-dodecaborane. Literatur ab 1950. Literaturschluß: Ende 1975.
„Borverbindungen" 13 (Erg.-Werk Bd. 44)	Bor-Sauerstoff-Verbindungen, Teil 1. Literatur ab 1950. Literaturschluß: Ende 1975.
„Borverbindungen" 14 (Erg.-Werk Bd. 45)	Bor-Wasserstoff-Verbindungen, Teil 1. Literatur ab 1950. Literaturschluß: Ende 1975.
„Borverbindungen" 15 (Erg.-Werk Bd. 46)	Amin-borane. Literatur ab 1950. Literaturschluß: Ende 1975.
„Borverbindungen" 16 (Erg.-Werk Bd. 48)	Bor-Sauerstoff-Verbindungen, Teil 2. Literatur ab 1950. Literaturschluß: Ende 1975.
„Borverbindungen" 17 (Erg.-Werk Bd. 51)	Borazin und seine Derivate. Literatur ab 1950. Literaturschluß: Ende 1976.
„Borverbindungen" 18 (Erg.-Werk Bd. 52)	Bor-Wasserstoff-Verbindungen, Teil 2. Literatur ab 1950. Literaturschluß: Ende 1976.
„Borverbindungen" 19 (Erg.-Werk Bd. 53)	Bor-Halogen-Verbindungen, Teil 2. Literatur ab 1950. Literaturschluß: Ende 1976.
„Borverbindungen" 20 (Erg.-Werk Bd. 54)	Bor-Wasserstoff-Verbindungen, Teil 3 Literatur ab 1950. Literaturschluß: Ende 1976.

Als Abschluß erscheinen eine systematische Aufstellung der einzelnen Kapitel und das Register für sämtliche Bände.

Table of Contents

Bor-Wasserstoff-Verbindungen, Teil 3

1 Pentaborane Species

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1.1 General Introduction

General Introduction

The present chapter deals with neutral and ionic boron-hydrogen species containing five boron atoms in the unit and including their derivatives.

The neutral species B_5H_9 (chapter 1.4, p. 11/22) and B_5H_{11} (chapter 1.2, p. 1/10) as well as adducts of the type $L_2 \cdot B_5H_9$ (L = monodentate ligand, chapter 1.5, p. 22/6) have been known for a long time. On the other hand, the ions $[B_5H_{12}]^-$ (chapter 1.9, p. 50/1), $[B_5H_{10}]^-$ (chapter 1.8, p. 49), and $[B_5H_8]^-$ (chapter 1.7, p. 46/9) are of relatively recent vintage. Included in the present chapters are all derivatives of the preceding except halogenated species. Partially halogenated pentaboron molecules and ions are described in Erg.-Werk, Vol. 45, "Borverbindungen" 14, p. 236/53. For metal derivatives of pentaborane species, see Erg.-Werk, Vol. 19 "Borverbindungen" 3, p. 190/2; for $B_5[N(CH_3)_2]_7$, see Erg.-Werk, Vol. 22 "Borverbindungen" 4, p. 281.

1.2 Pentaborane(11), B_5H_{11}

B_5H_{11}

See also system number 13 "Bor", p. 63, and "Bor" Erg.-Bd., p. 118/9.

1.2.1 Preparation

Preparation

Pentaborane(11) is prepared in a concentric tube hot-cold reactor by pyrolyzing B_4H_{10} [1, 2], B_2H_6 [2 to 6], or a mixture of B_4H_{10} and B_2H_6 [2, 7, 8]. The conditions which optimize the formation of B_5H_{11} must take into account the thermal instability of B_5H_{11} [1, 9 to 11] and the fact that B_4H_{10} is an intermediate when the preparation involves the conversion of B_2H_6 to B_5H_{11} [2, 11 to 14].

B_5H_{11}
Preparation

A reactor, charged with B_2H_6 and operating at an outer wall temperature of −30°C and an inner wall temperature of 120°C, produced B_4H_{10} initially which, in turn, was converted to B_5H_{11} and H_2 according to the equation: $5\,B_4H_{10} \rightarrow 4\,B_5H_{11} + 3\,H_2$. A 70% yield (1 g) of B_5H_{11} was obtained in a 150 min reaction period, and only small quantities of higher boranes were formed when the products B_5H_{11} and H_2 were removed periodically from the reactor while the B_2H_6 pressure was maintained [2]. Although the thermal conversion is independent of B_2H_6 pressure [13], the presence of B_2H_6 is important [2, 7, 8] in order to minimize the decomposition of B_5H_{11} in the following equilibrium system [11, 14]: $B_5H_{11} + H_2 \rightleftharpoons 2\,B_4H_{10} + B_2H_6$. Pyrolytic procedures for the preparation of B_5H_{11}, involving flow methods [15 to 17] and static methods [1, 11, 18, 19] have been utilized. These methods are successful only when the formation of the very difficult to separate B_5H_9 is minimized. Variations on the pyrolytic procedures as well as the effects of solvents and potential catalysts on the conversion of B_2H_6 to B_5H_{11} are described in several reports to the U.S. Government; these reports have been summarized [20].

A convenient high-yield synthesis of B_5H_{11}, which does not require pyrolytic procedures [21, 22] but is dependent upon a source of B_4H_{10}, has been developed. Preparative reactions are: $B_4H_{10} + KH \xrightarrow[(C_2H_5)_2O]{-78°C} K[B_4H_9] + H_2$; $K[B_4H_9] + {}^1/_2\,B_2H_6 \xrightarrow[(C_2H_5)_2O]{-35°C} K[B_5H_{12}]$; $K[B_5H_{12}] + HCl\,(liquid) \xrightarrow{-110°C} B_5H_{11} + H_2 + KCl$. The first two reactions are quantitative and yields of B_5H_{11} are typically 58 to 70% overall [21 to 25].—Other reactions which yield B_5H_{11} are given in table 1/1.

Table 1/1
Reactions Leading to the Formation of B_5H_{11}.

Reactants	% Yield	Comments	Lit.
B_2H_6 (N_2 diluent)	74	7.9% conversion using a 175°C flow reactor with zirconium boride catalyst	[26]
B_2H_6	30	20 to 50% conversion using silent electrical discharge	[27]
$THF \cdot B_3H_7 + BF_3 + CO$	0.26	$OC \cdot B_3H_7$ principal product	[28]
$(CH_3)_2O \cdot B_3H_7$	29	Principal product B_4H_{10}	[29]
$[(CH_3)_4N][B_3H_8] + (HPO_3)_n$	14	Mixture of B_5H_9 and B_5H_{11}, principal product B_4H_{10}	[30]
$OC \cdot B_4H_8 + B_2H_6$	75	30% in the absence of B_2H_6	[31]
$(CH_3)B_5H_{10} + B_2H_6$	72	10% in the absence of B_2H_6	[7]
B_2H_6 (184.9 nm Hg line)	—	1% or less conversion B_4H_{10} and nonvolatile $(BH)_n$ are other products	[32]

Pentaborane(11) has been separated from boron hydrides other than B_5H_9 by vacuum line trap-to-trap distillations. Slow passage of vapors through traps kept at −63, −65 to −95, −135, and −196°C results in the condensation of a mixture of B_5H_{11} and B_5H_9 in the −65 to −95°C traps [1, 11, 13, 27, 33, 34]. Separation of B_5H_{11} from B_5H_9 has been accomplished by repeated slow passage of the vapors through a trap maintained at −78°C [27, 33] with B_5H_{11} remaining in the trap. Residual B_6H_{10} can be separated from B_5H_{11} by passing the mixture, quickly, through a trap at −63°C; the B_6H_{10} is retained in the trap [27]. Low temperature fractional distillation columns [31, 35 to 37] have been successfully used to separate B_5H_{11} from other boron hydrides [28, 38] and from reaction mixtures containing $OC \cdot B_4H_8$ [39, 40]. A codistillation-fractionation apparatus separates B_5H_{11} quantitatively from B_2H_6, B_4H_{10}, and B_6H_{10} [41].