

Gmelin Handbook of Inorganic Chemistry

8th Edition

B

Boron Compounds

3rd Supplement Volume 1

Boron and Hydrogen

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8th Edition

B **Boron Compounds**

3rd Supplement Volume 1

Boron and Hydrogen

With 142 illustrations

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8th Edition

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Preface

The 3rd supplement continues the updating of the original 20 volumes on boron compounds published between 1974 and 1979. The first supplement to this series brought the literature closing date uniformly to the end of 1977, whereas the two volumes of the 2nd supplement have extended the literature coverage of boron compounds to 1980. Selection and presentation of data parallel the style selected for the two previous supplement volumes, which appeared in 1980/1 and 1982/3, respectively. The Gmelin Principle of the Last Position is largely adhered to, excepting substituted polyboron species containing boron-boron bonds (all of which are found in Chapter 2 within the system boron-hydrogen). The literature is considered through 1984.

Volume 1 of the present 3rd supplement contains the systems boron-noble gases and boron-hydrogen; Volume 2 the system boron-oxygen. Volume 3 will contain the systems boron-nitrogen, boron-fluorine, and boron-bromine; the remaining systems and a formula index will be included in the final 4th volume of this supplement.

The two chapters of the present volume describing "Boron and Noble Gases" and "Boron and Hydrogen" are from Professor T. Onak (Los Angeles) and Professor L. Barton (St. Louis), respectively. Selected data on metal derivatives are included whenever these contribute to the appreciation and understanding of the principal systems. An additional section in the borane chapter deals with the nomenclature of the boron polyhedra and describes a new approach for naming these compounds. The new system gives more clarity to the naming of *closo*-boranes and especially the *nido*- and *arachno*-systems derived from them.

Unless otherwise noted, a positive sign for the chemical shifts of nuclear magnetic resonance signals indicates downfield from the references $(\text{CH}_3)_4\text{Si}$ for ^1H and ^{13}C NMR, $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{BF}_3$ for ^{11}B NMR, aqueous NaNO_3 for ^{14}N NMR, and CFCl_3 for ^{19}F NMR. Some of the more recent IUPAC recommendations are followed, e.g., abbreviations for complexed solvents are in lower case.

We express our thanks to Professor Dr. Kurt Niedenzu (Department of Chemistry, University of Kentucky, Lexington, Kentucky, USA), the initiator and guiding spirit of the boron series of Gmelin Handbook, who did a tremendous amount of work in convening the authors of the chapters, editing, improving, and checking the contents of the present (and all of the former) volumes of this special part of Gmelin Handbook.

Frankfurt am Main
April 1987

Karl-Christian Buschbeck

Boron and Boron Compounds in the Gmelin Handbook (Syst. No. 13)

- "Bor" (Main Volume) 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 1) Occurrence. The Element. Compounds of B with H, O, N, the Halogens, S, and C.
Literature closing date: end of 1949.
- "Borverbindungen" 1 Boron Nitride. B-N-C Heterocycles. Polymeric B-N Compounds.
Literature coverage from 1950 up to 1972.
- "Borverbindungen" 2 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 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 Compounds with Isolated Trigonal Boron Atoms and Covalent Boron-Nitrogen Bonding (Aminoboranes and B-N Heterocycles).
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- "Borverbindungen" 5 Boron-Pyrazole. Derivatives and Spectroscopic Studies on Trigonal B-N Compounds.
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- "Borverbindungen" 6 Carboranes, Part 2. Hetero- and Metallocarboranes. Polymeric Carborane Derivatives. Electronic Properties.
Literature coverage from 1950 up to 1974 or 1971, respectively.
- "Borverbindungen" 7 Boron Oxides. Boric Acids. Borates.
Literature coverage from 1950 to the end of 1973.
- "Borverbindungen" 8 The Tetrahydroborate Ion and Its Derivatives.
Literature coverage from 1950 to the end of 1974.
- "Borverbindungen" 9 Boron-Halogen Compounds, Part 1.
Literature coverage from 1950 to the end of 1974.
- "Borverbindungen" 10 Boron Compounds with Coordination Number 4.
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- "Borverbindungen" 11 Carboranes, Part 3. Dicarba-*closo*-dodecaboranes.
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- "Borverbindungen" 19 Boron-Halogen Compounds, Part 2.
Literature coverage from 1950 to the end of 1976.
- "Borverbindungen" 20 Boron-Hydrogen Compounds, Part 3.
Literature coverage from 1950 to the end of 1976.
- "Boron Compounds" Formula Index
(for the volumes "Borverbindungen" 1 to 20).
- "Boron Compounds"
1st Suppl. Vol. 1 Boron and Rare Gases. Boron and Hydrogen.
Boron and Oxygen
Literature coverage through 1977.
- "Boron Compounds"
1st Suppl. Vol. 2 Boron and Nitrogen, Boron and Halogens.
Literature coverage through 1977.
- "Boron Compounds"
1st Suppl. Vol. 3 Boron and Chalcogens. Carboranes.
Formula Index for 1st Suppl. Vol. 1 to 3.
Literature coverage through 1977.
- "Boron Compounds"
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Boron and Nitrogen. Formula Index.
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Formula Index.
Literature coverage through 1980.
- "Boron Compounds"
3rd Suppl. Vol. 1 Boron and Hydrogen (present volume)
Literature coverage through 1984.
- "Boron Compounds"
3rd Suppl. Vol. 2 Boron and Oxygen
Literature coverage through 1984.

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1 The System Boron-Noble Gases

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This chapter, which covers the period 1981 through 1984, continues the earlier presentations appearing in "Borverbindungen" 10, 1976, pp. 270/2; "Boron Compounds" 1st Suppl. Vol. 1, 1980, p. 1; "Boron Compounds" 2nd Suppl. Vol. 1, 1983, pp. 1/2.

A high energy boron-helium complex may be implicated in a study concerning a one-electron capture process as a result of low velocity (1.3 to 2.3×10^7 cm/s) collisions between B^{3+} and He to give B^{2+} and He^+ [1].

Features at 945 and 987 cm^{-1} in the infrared photodissociation spectrum of $Ar \cdot BCl_3$ are attributed to the selective photodissociation of the $Ar \cdot ^{11}BCl_3$ and $Ar \cdot ^{10}BCl_3$ species, respectively. The predissociation lifetime of the v_3 excited state observed in the one-photon infrared dissociation of $Ar \cdot BCl_3$ is between 1 and 3 ps [2]. This short lifetime of $Ar \cdot BCl_3$ is justified by a Monte Carlo-RRKM calculation; it is suggested that energy randomization among the low frequency modes of oscillation may play an important role in the predissociation dynamics [3].

From SCF and CI calculations of the potential energy curves and non-adiabatic coupling matrix elements $\langle \alpha | \partial / \partial R | \beta \rangle$ for the three lowest Σ states of ArB indicate that there is extensive mixing of the $B(2p_z)$, $B(3s)$ and $B(3p_z)$ states around 3.4 a.u.; the resulting $1\Sigma/2\Sigma$ crossing is located 6.6 eV above the ground state entrance channel. The Rydbergisation of the $4a$ valence orbital is essentially complete inside the avoided crossing. The 3Σ state comes within 1.9 eV of the 2Σ state in this region and thus all three states would have to be included in a dynamical treatment of the system at collision energies much above 10 eV [4].

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2 The System Boron-Hydrogen

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2.1 Introduction

This chapter, which covers the period 1981 through 1984, continues the treatment found in "Boron Compounds" 2nd Suppl. Vol. 1, 1983, pp. 3/204. In order to be consistent with the latter, the presentation adheres to the Gmelin Principle of the Last Position for B_1 species; and for species containing two or more connected boron atoms, all derivatives are included in the present chapter.

The period under consideration has been a very active one in boron hydride chemistry. The session lectures from the Fifth International Meeting on Boron Chemistry have been published [1]. The bonding and systematics of boranes and related cluster systems continue to attract significant attention. Notably Stone published a theory of bonding for all approximately spherical clusters, called "tensor surface harmonic theory", and applied it to boranes [2 to 5]. The method yields a proof of the electron counting rules for boranes and other cluster systems (polyhedral skeletal electron pair theory) which have been reviewed recently by Wade [6] and by Mingos [7], who developed them. An alternative approach has been suggested invoking a bireciprocal length-energy relationship which is used to predict structures and rearrangements of boranes [8 to 12]. Other theoretical studies have been applied to the *closo*-boranes including a topological approach which explains the fluxionality in the B_5 , B_8 , B_9 , and B_{11} systems on the basis of the presence of degenerate edges in the polyhedron, and another which uses graph theory to elucidate the stability of the perhalogenated neutral species [13, 14]. Also, studies have applied structure-resonance theory in order to describe valence structures of boranes [15] and calculated directly heats of formation by the molecular orbital-bond index method [16]. Finally, Lipscomb has reviewed his own work on electron-correlation effects in boron hydride structures, intermediates, and reactions [17].

The systematization and structures of the boranes and related clusters have been reviewed [18, 19], a general review of boranes has been presented [20], new methods of synthesis of boranes based on hydride abstraction reactions have been described [21], and a review of ^{11}B NMR spectroscopy of boranes has appeared [22]. The chemistry of metallaboranes has received considerable attention as evidenced by the number of reviews which have appeared since 1980. These include reviews of the whole field [23 to 26], of individual investigators' work [27 to 31], and of the relationship between metallaboranes and metal hydrocarbon complexes [32].

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2.2 Nomenclature of Borane Polyhedra

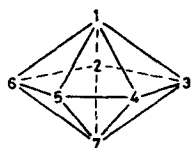
This section describes a new approach to the nomenclature of polyhedral boranes. A four-part structural descriptor uniquely defining polyboron deltahedra with at least one rotational symmetry axis and at least one plane of symmetry is proposed [1]. The system removes many of the ambiguities involved in the naming of *closo*-boranes and especially the *nido* and *arachno* systems derived from them. A brief description of the system is given herein and examples are drawn from polyhedra with 4 to 13 vertices, thus covering almost all the known borane and related systems. The four-part structural descriptor is composed of: a) the Schoenflies point group symmetry symbol for the homogeneous boron polyhedron from which all substituents and/or ligands have been removed from each vertex. The symbol assigned is based on an idealized closed deltahedral structure; b) an indication of the arrangement and type of vertices present in the polyhedron. A series of Arabic numbers giving the number of vertices with the same skeletal connectivity, in planes that are perpendicular to the reference axis, is used. The numbers are cited in the order that the planes they define are preferred for numbering (see below). Each Arabic number is followed by a symbol v^n where n is a superscript describing the number of polyhedral edges connected to each of the vertices, i.e., the skeletal connectivity. The Arabic numbers are enclosed in parentheses after a hyphen which follows the point group symmetry symbol and the first number within the parentheses is the vertex or vertices at which

numbering commences. The sum of the Arabic numbers is the total number of vertices in the polyhedron; c) a symbol following the parentheses at the terminus of the series of Arabic numbers and the associated designations v^n separated by a hyphen indicating the number of triangular faces in the polyhedron, Δ^n ; and d) the designation *-closo*. Thus, the complete descriptor for the bicapped Archimedean antiprism, the structure of the basic polyhedron in $[B_{10}H_{10}]^{2-}$, is $[D_{4d}-(1v^44v^54v^51v^4)-\Delta^{16}-closo]$.

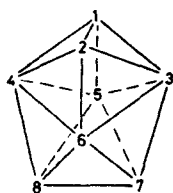
descriptor:	a) $n=4$ $[T_d-(1v^33v^3)-\Delta^4-closo]$ $[T_d-(13)-\Delta^4-closo]$	b) $n=5$ $[D_{3h}-(1v^33v^41v^3)-\Delta^6-closo]$ $[D_{3h}-(131)-\Delta^6-closo]$	c) $n=6$ $[O_h-(1v^44v^41v^4)-\Delta^8-closo]$ $[O_h-(141)-\Delta^8-closo]$
reference axis:	1-(2, 3, 4)	1-5	1-6
reference plane:	1-2-(3, 4)	1-2-(3, 4)-5	1-(2, 5)-(3, 4)-6
h) $n=9$ $[C_{2v}-(1v^64v^422)-\Delta^{14}-closo]$	i) $n=9$ $[C_{2v}-(1v^42v^42v^622v^4)-\Delta^{14}-closo]$	j) $n=10$ $[D_{4d}-(1v^4441v^4)-\Delta^{16}-closo]$ $[D_{4d}-(1441)-\Delta^{16}-closo]$	k) $n=10$ $[C_{3v}-(1v^63v^433)-\Delta^{16}-closo]$
1-(8, 9) 1-6-7-(8, 9)	1-(8, 9) 1-2-3-6-7-(8, 9)	1-10 1-2-4-(6, 9)-(7, 8)-10	1-(8, 9, 10) 1-2-6-8-(9, 10)

Fig. 2-1. Proposed structural descriptors for

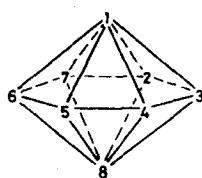
Some simplification of this descriptor is suggested by the authors. Since the connectivity of vertices in boron polyhedra is often 5, the symbol v^n is omitted when $n = 5$. Thus, the 10-vertex polyhedron becomes $[D_{4d}-(1v^441v^4)-\Delta^{16}\text{-clos}]$. A further simplification omits the v^n symbol when $n = 3$ and 4 for the common polyhedra with 12 or fewer vertices. Thus, the D_{4d} bicapped Archimedean antiprism becomes $[D_{4d}-(1441)-\Delta^{16}\text{-clos}]$. The proposed descriptors for the $n = 4$ to 13 polyhedra are given in Fig. 2-1 along with those including only the omission of the v^5 symbol.

d) $n = 7$ $[D_{5h}-(15v^41)-\Delta^{10}\text{-clos}]$ $[D_{5h}-(151)-\Delta^{10}\text{-clos}]$ 

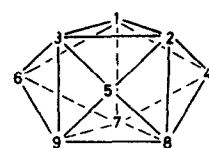
1-7
1-2-(4,5)-7

e) $n = 8$ $[D_{2d}-(2v^4222v^4)-\Delta^{12}\text{-clos}]$ $[D_{2d}-(2222)-\Delta^{12}\text{-clos}]$ 

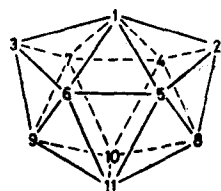
(1,2)-(7,8)
1-2-5-6-(7,8)

f) $n = 8$ $[D_{6h}-(1v^66v^41v^6)-\Delta^{12}\text{-clos}]$ $[D_{6h}-(1v^661v^6)-\Delta^{12}\text{-clos}]$ 

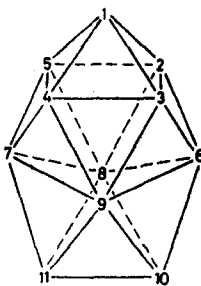
1-8
1-(2,7)-(4,5)-8

g) $n = 9$ $[D_{3h}-(33v^43)-\Delta^{14}\text{-clos}]$ $[D_{3h}-(333)-\Delta^{14}\text{-clos}]$ 

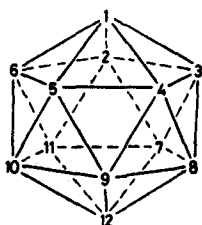
(1,2,3)-(7,8,9)
1-(2,3)-5-7-(8,9)

h) $n = 11$ $[C_{2v}-(1v^62v^4422)-\Delta^{18}\text{-clos}]$ 

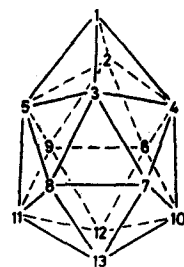
1-(10,11)
1-(4,7)-(5,6)-10-11
1

m) $n = 11$ $[C_{2v}-(1v^4422v^62v^4)-\Delta^{18}\text{-clos}]$ 

1-(10,11)
1-(2,5)-(3,4)-8-9-(10,11)

n) $n = 12$ $[I_h-(1551)-\Delta^{20}\text{-clos}]$ 

1-12
1-2-(4,5)-(7,11)-9-12

o) $n = 13$ $[C_{2v}-(1v^422v^6422)-\Delta^{22}\text{-clos}]$ 

1-(12,13)
1-2-3-(6,9)-(7,8)-12-13

polyboron polyhedra $[B_nH_n]^{2-}$ ($n = 4$ to 13) [1].