

Gmelin Handbook of Inorganic Chemistry

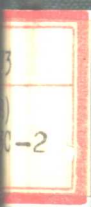
8th Edition

B

Boron Compounds

3rd Supplement Volume 2

Boron and Oxygen



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Gmelin Handbook of Inorganic Chemistry

8th Edition

B **Boron Compounds**

3rd Supplement Volume 2

Boron and Oxygen

With 39 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). Examples of organic derivatives are included, especially in those cases where the carbon-free species are not known; and the carboranes are treated comprehensively. The literature is considered through 1984.

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

The first chapter of the present volume on the compounds of boron and oxygen provides sections on the binary boron oxides, including some radicals, and the anhydrous borate ions. The following chapter describes boron-oxygen compounds with hydrogen or organyl groups. The most extended section in this part is that on orthoboric acid, H_3BO_3 ; the other sections here are on oxyborane, HBO and HOB, and related species, derivatives of hydroxyborane, H_2BOH , monomeric metaboric acid, HBO_2 , peroxoboranes, diboryloxides, and boroxines. The description of the hydrated borate ions, which in most cases contain OH groups primarily refers to their occurrence in the respective salts.

The table of borate minerals updates the corresponding tables in the previous supplements.

Lexington, Kentucky
Frankfurt am Main
November 1986

Kurt Niedenzu
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).
Literature coverage from 1950 to the end of 1973.
- "Borverbindungen" 5 Boron-Pyrazole. Derivatives and Spectroscopic Studies on Trigonal B-N Compounds.
Literature coverage from 1950 to the end of 1973.
- "Borverbindungen" 6 Carboranes, Part 2. Hetero- and Metallocarboranes. Polymeric Carborane Derivatives. Electronic Properties.
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- "Borverbindungen" 7 Boron Oxides. Boric Acids. Borates.
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- "Borverbindungen" 8 The Tetrahydroborate Ion and Its Derivatives.
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Literature coverage from 1950 to the end of 1974.
- "Borverbindungen" 10 Boron Compounds with Coordination Number 4.
Literature coverage from 1950 to the end of 1975.
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Literature coverage from 1950 to the end of 1975.

- "Borverbindungen" 12 Carboranes, Part 4. Dicarba-closo-dodecaboranes.
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- "Boron Compounds" Formula Index
(for the volumes "Borverbindungen" 1 to 20).
- "Boron Compounds" Boron and Rare Gases. Boron and Hydrogen.
1st Suppl. Vol. 1 Boron and Oxygen
Literature coverage through 1977.
- "Boron Compounds" Boron and Nitrogen, Boron and Halogens.
1st Suppl. Vol. 2 Literature coverage through 1977.
- "Boron Compounds" Boron and Chalcogens. Carboranes.
1st Suppl. Vol. 3 Formula Index for 1st Suppl. Vol. 1 to 3.
Literature coverage through 1977.
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- "Boron Compounds" Boron and Halogens. Boron and Chalcogens. Carboranes.
2nd Suppl. Vol. 2 Formula Index.
Literature coverage through 1980.
- "Boron Compounds" Boron and Oxygen (present volume)
3rd Suppl. Vol. 2 Literature coverage through 1984.

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3 The System Boron-Oxygen

Gert Heller

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3.1 General Remarks

Boron-Oxygen Compounds in the Gmelin Handbook

"Bor" 1926, pp. 64/104, 136, 141/2; "Bor" Erg.-Bd. 1, 1954, pp. 123/59, 222/35; "Borverbindungen" 7, 1975, pp. 1/237, "Borverbindungen" 8, 1976, pp. 53/65, 106/46, 217/20, "Borverbindungen" 13, 1977, pp. 1/48, 115/239, "Borverbindungen" 16, 1977, pp. 1/14, 24/100, 124/221; "Boron Compounds" 1st Suppl. Vol. 1, 1980, pp. 113/316; "Boron Compounds" 2nd Suppl. Vol. 1, 1983, pp. 205/303.

New Summary Accounts

Reviews on the toxicology of materials containing boron-oxygen bonds [1], and on the comparative toxicity of H_3BO_3 and some borates [2] have been compiled.

References for 3.1:

- [1] F. R. Robinson (BNL-51118 [1980] 157/63 from C.A. 95 [1981] No. 163132).
- [2] A. A. Silaev (Vopr. Gigieny Truda Svyazis Nov. Tekhnol. Protsessami Mashinostr. Khim. Promsti. 1982 108/11; C.A. 98 [1983] No. 156002).

3.2 Binary Species

3.2.1 Boron Oxides

This presentation continues the treatment in "Boron Compounds" 2nd Suppl. Vol. 1, 1983, pp. 205/15.

3.2.1.1 The Monoboron Monooxide Radical, $BO^\bullet$

Formulas of radicals (like those of other compounds) are written according to the regulations of IUPAC [36].

Inert-gas ion impact on elemental boron and B_2O_3 in the presence of H_2 or O_2 results in oxygen-photon signals in the visible region. Independent of the gas present, B_2O_3 yields unresolved radiation, coinciding with the general region of the $A^2\Pi-X^2\Sigma^+$ system of $BO^\bullet$ [1]. In the single-collision reactions of boron atoms with O_2 , SO_2 , N_2O , NO_2 , or H_2O_2 , the electronically excited $A^2\Pi$ state of $BO^\bullet$ has been observed. The cross-sections for the reactions with O_2 , SO_2 , N_2O , NO_2 , and H_2O_2 are, respectively, 0.048; 0.0078; 0.01; 0.023; and 0.005 Å² [2]. Chemiluminescence from the electronically excited $A^2\Pi$ state of $BO^\bullet$ has been observed in the single-collision reactions of boron atoms with several epoxides, e.g., C_3H_6O ; the formation is exoergic by 4.65 eV; without the C=C bond formation energy of 2.07 eV, the required minimum energy is 2.92 eV. For the reaction $B + C_3H_6O$, the cross-section for the production of the $A^2\Pi$ state of $BO^\bullet$ is 0.0067; for the reaction with C_4H_8O it is 0.0045; for C_4H_8O 0.0064; for $C_4H_6O_2$

0.0055; for C_3H_5FO 0.0047; for C_3H_5ClO 0.0024; for C_3H_5BrO 0.0027; and for $C_3H_3Cl_3O$ 0.0005 $\text{\AA}^2$. The vibrational distributions in the $A^2\Pi$ state have been determined for the reaction $B + C_3H_6O$ (see Table 3/1) [3].

Table 3/1

Relative Populations of the Electronic Levels $v' = 0$ to $v' = 5$ in the $A^2\Pi$ State, Nv' , and the Total Cross-Sections $\sigma v'$ for the Formation of Those States [3].

v'	0	1	2	3	4	5
Nv'	1	0.642	0.344	0.159	0.0758	0.036
$\sigma v'$ in $\text{\AA}^2$	0.0027	0.0018	0.0012	0.00068	0.00032	0.00016

Chemiluminescence studies were performed under single-collision conditions in a beam-gas apparatus for the reactions of boron atoms (cross-sections in $\text{\AA}^2$) with C_2H_4O (0.0073), C_3H_6O (0.0070), C_4H_8O (0.0052), diepoxybutane (0.0061), cyclopentene oxide (0.0044), cyclohexene oxide (0.0038), 3-vinylcyclohexene oxide (0.0044), and styrene oxide (0.0065). The nascent vibrational distributions in the electronically excited $A^2\Pi$ state of BO^* were determined. These distributions are in good agreement with a statistical model which assumes that only those modes of the polyatomic product are excited which correspond to the conformation change in the transition from the reacting epoxide to the alkene product [4].

Boron atoms react with water vapor to yield chemiluminescence corresponding to the $A^2\Pi \rightarrow X^2\Sigma^+$ transition of BO^* . The bimolecular reaction, which was studied under single-collision conditions ($p(\text{oxidant}) = 1$ to 4×10^{-4} Torr), must involve the simultaneous formation of BO^* ($A^2\Pi$) and H_2 ($^1\Sigma_g^+$); no evidence for $(HBOH)^*$ formation was obtained. Under multiple-collision conditions ($p(\text{total}) \approx 950$ to $100 \mu\text{m}$, $p(\text{oxidant}) \approx 55 \mu\text{m}$), vibrational relaxation is observed which is significantly more pronounced than that characterizing similar studies involving reactions of boron with O_2 , N_2O , or NO_2 . In consonance with previous studies, evidence for differing $A^2\Pi_{1/2} \rightarrow X^2\Sigma^+$ and $A^2\Pi_{3/2} \rightarrow X^2\Sigma^+$ transition moments and $A^2\Pi_{1/2}$ E-V quenching was obtained; these results are explained in terms of substantial $A^2\Pi_{1/2} \rightarrow X^2\Sigma^+$ mixing. There is a high barrier of ca. 20 kcal/mol for the formation of the ground electronic $^2\Sigma^+$ state of BO^* [5].

A thermokinetic method has been used to study the interaction of O_2 with purified boron powder at high temperatures and to determine different values of the specific powder surface area [6]. The reaction of BCl_3 with oxygen atoms has been used to produce $BO^* X^2\Sigma^+$ radicals in order to study them in a fast-flow reactor. Laser-induced fluorescence has been used to follow the $BO^* X^2\Sigma^+$ radicals with the transition $A^2\Pi \rightarrow X^2\Sigma^+$ at 425 nm. The feasibility of kinetic studies on these radicals has been demonstrated by a kinetic study of the reaction $BO^* + O_2 \rightarrow (BO_2)^* + O$, giving a rate coefficient $k_1 = 4.4(\pm 3.2) \times 10^{-12} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at 295 K [7].

At ambient temperatures, atomic oxygen (3P) atoms attack $(CH_3)_3N-BH_3$ initially at the BH_3 moiety to displace the amine. The subsequent attack on BH_2 and BH generates highly excited BO^* ($A^2\Pi$, $v \leq 11$) which is the source of chemiluminescence. The rate of destruction of $(CH_3)_3N-BH_3$ is $k_2 = 4 \times 10^{10}$ to $1.4 \times 10^9 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ and is two orders of magnitude faster as compared with $OC-BH_3$ [8]. The chemiluminescence which is generated on reaction of $L-BH_3$ ($L = N(CH_3)_3$, $N(C_2H_5)_3$, pyridine, CO, tetrahydrofuran, or $S(CH_3)_2$) with oxygen atoms shows the extensive α -band system of BO^* [9, 35].

BO^* (besides B_2O_2 and B_2O_3) is a desorption product of oxygen interaction with LaB_6 single crystals [10]. When a mixture of boron and Nb_2O_5 is heated with a plasma arc, BO^* and NbB_2 must have been formed, since hydrolysis by atmospheric moisture leads to H_3BO_3 [11]. B_4C reacts with CO gas in order to form solid C and, ultimately, B_2O_3 gas; one of the first products is

BO* [12]. A sputter ion source was used for the production of boron monoxide ions from a solid [34].

The perturbations of the rotational structure of the ($v' = 4, v'' = 17$) band of the $A^2\Pi_{1/2} \rightarrow X^2\Sigma^+$ system for the boron-11 monoxide radical has been observed in the blended (R_2, Q_{21}) and (Q_2, P_{21}) branches, as well as in the unblended P_2 and R_{21} branches with maximal deviations of 0.60 cm^{-1} . Analysis of these data using the effective $^2\Pi$ and $^2\Sigma^+$ Hamiltonian matrices gave the deperturbed set of molecular rotational constants. The A-X electronic perturbation matrix elements, $\mathcal{H}_{el}^{SO}$ and $\mathcal{H}_{el}^{RE}$, are $-55.20(63)$ and $+0.489(28)$, respectively, which are dissimilar in magnitude for $^{11}\text{BO}^*$ and the isoelectronic CN^* radical [13]; 16 bands of the same system of $^{11}\text{BO}^*$ and 13 bands of $^{10}\text{BO}^*$ show no perturbations [14].

The potential energy curve for the lowest states of BO^* has been calculated with the complete active space SCF (CASSCF) method. The result has been compared with previous ab-initio calculations and available experimental data (Table 3/2).

Table 3/2
Spectroscopic Characteristics for the BO^* States [15].

state	Ref.	minimum R_e in Å	D_e in eV	ω_e in cm^{-1}	T_e in cm^{-1}	R_m in Å	ΔE in cm^{-1}
$^2\Sigma^+$	[15]	1.22	7.97	1909	0	—	—
	[16]	1.21	—	1873	0	—	—
	exp	1.20	8.33	1886	0	—	—
$^2\Pi$	[15]	1.38	—	1238	25401	—	—
	[16]	1.36	—	1289	21882	—	—
	exp	1.35	—	1261	23834	—	—
$^2\Delta$	[15]	1.55	0.83	1231	55471	2.13	4920
$^4\Sigma^+$	[15]	1.36	2.04	1279	46738	2.76	1260
$^4\Pi$	[15]	1.30	—	1558	56668	1.54	13678
$^4\Delta$	[15]	1.44	1.38	1140	52829	2.27	2529

The CASSCF method has also been applied to some excited states of the BO^* molecule. Only portions of the full potential curves could be obtained via the usual two-step procedure. Table 3/3 shows the configuration state function coefficients for the BO^* states [15].

Table 3/3
Configuration State Function Coefficients for the BO^* States (coefficient is omitted if its magnitude is less than 0.1; CSF's with asterisk differ in the spin-coupling scheme) [15].

state	CSF	R (in a.u.)			
		2.5	3.5	5.0	10.0
$^2\Sigma^+$	$4\sigma^2 5\sigma 1\pi_x^2 1\pi_y^2$	0.961	0.918	—	—
	$4\sigma 5\sigma^2 1\pi_x^2 1\pi_y^2$	—	—	0.588	0.596
	$4\sigma 5\sigma^2 1\pi_x 2\pi_x 1\pi_y^2$	—	—	0.464	—
	$4\sigma^2 5\sigma 2\pi_x^2 1\pi_y^2$	-0.110	-0.120	—	—

Table 3/3 (continued)

state	CSF	R (in a.u.)			
		2.5	3.5	5.0	10.0
	$4\sigma 5\sigma^2 2\pi_x^2 1\pi_y^2$	—	—	-0.155	—
	$4\sigma 5\sigma^2 1\pi_x^2 1\pi_y 2\pi_y^*$	—	—	—	-0.421
	$4\sigma 5\sigma^2 1\pi_x^2 1\pi_y 2\pi_x^*$	—	—	0.464	0.243
	$4\sigma 5\sigma^2 1\pi_x 2\pi_x 1\pi_y 2\pi_y$	—	—	-0.281	—
	$4\sigma^2 5\sigma 1\pi_x^2 2\pi_y^2$	-0.110	-0.120	—	—
	$4\sigma 5\sigma^2 1\pi_x^2 2\pi_y^2$	—	—	-0.155	-0.594
$^2\Pi$	$4\sigma^2 5\sigma^2 1\pi_x 1\pi_y^2$	0.962	0.951	0.828	0.601
	$5\sigma^2 6\sigma^2 1\pi_x 1\pi_y^2$	—	—	-0.275	-0.589
	$4\sigma 5\sigma^2 6\sigma 1\pi_x 1\pi_y^*$	—	—	-0.237	0.486
	$4\sigma 5\sigma^2 6\sigma 1\pi_x 1\pi_y^*$	—	—	-0.122	—
	$4\sigma^2 1\pi_x 2\pi_x^2 1\pi_y^2$	0.184	0.179	0.140	—
	$4\sigma^2 5\sigma^2 1\pi_x 1\pi_y 2\pi_y$	—	—	0.162	—
	$4\sigma 5\sigma^2 6\sigma 1\pi_x 1\pi_y 2\pi_y$	—	—	0.237	—
$^2\Delta$	$4\sigma^2 5\sigma 1\pi_x 1\pi_y^2 2\pi_y^*$	0.862	0.792	—	—
	$4\sigma^2 5\sigma 1\pi_x 1\pi_y^2 2\pi_y^*$	0.494	0.561	—	—
	$4\sigma 5\sigma^2 1\pi_x 1\pi_y^2 2\pi_y$	—	—	0.971	0.972
	$4\sigma 6\sigma^2 1\pi_x 1\pi_y^2 2\pi_y$	—	—	-0.159	-0.166
	$4\sigma 1\pi_x 2\pi_x^2 1\pi_y^2 2\pi_y$	—	—	0.166	0.166
$^4\Sigma^+$	$4\sigma^2 5\sigma 1\pi_x 2\pi_x 1\pi_y^2$	0.694	0.673	—	—
	$4\sigma 5\sigma^2 1\pi_x 2\pi_x 1\pi_y^2$	—	—	0.971	0.972
	$4\sigma 6\sigma^2 1\pi_x 2\pi_x 1\pi_y^2$	—	—	-0.159	-0.166
	$4\sigma^2 5\sigma 1\pi_x^2 1\pi_y 2\pi_y$	0.694	0.673	—	—
	$4\sigma 1\pi_x 2\pi_x 1\pi_y^2 2\pi_y^2$	—	—	-0.163	-0.166
$^4\Pi$	$4\sigma 5\sigma 1\pi_x^2 2\pi_x 1\pi_y^2$	0.988	—	—	—
	$4\sigma^2 5\sigma^2 1\pi_x 1\pi_y 2\pi_y$	—	0.966	0.971	0.972
	$4\sigma^2 6\sigma^2 1\pi_x 1\pi_y 2\pi_y$	—	-0.104	-0.154	-0.163
	$4\sigma^2 1\pi_x 2\pi_x^2 1\pi_y 2\pi_y$	—	0.194	0.171	0.167
$^4\Delta$	$4\sigma^2 5\sigma 1\pi_x^2 2\pi_x 1\pi_y$	0.701	0.681	—	—
	$4\sigma 5\sigma^2 1\pi_x^2 2\pi_x 1\pi_y$	—	—	0.970	0.972
	$4\sigma 6\sigma^2 1\pi_x^2 2\pi_x 1\pi_y$	—	—	-0.158	-0.166
	$4\sigma^2 5\sigma 1\pi_x 1\pi_y^2 2\pi_y$	0.701	0.681	—	—
	$4\sigma 1\pi_x^2 2\pi_x 1\pi_y 2\pi_y^2$	—	—	-0.164	-0.166

It was possible to complete the curves and to consider other excited states by using an averaged field technique. The energies had been computed with orbitals that were self-consistently determined with first- and second-order density matrices averaged over several states [17]. The values, obtained by the CASSCF method for the BO_2^+ ion, have been compared with those obtained for BO^+ , e.g., for the state $^2\Sigma^+$ $R=2.33$ a.u., $D_e=8.04$ eV, and