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8th Edition

B
Boron Compounds

3rd Supplement Volume 4

Boron and Cl, Br, I, S, Se, Te. Carboranes

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With 19 illustrations

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Preface

The present Volume 4 of "Boron Compounds" 3rd Supplement concludes the 3rd supplement issue on boron compounds, but will be augmented by a separate index volume for the boron compounds discussed in the four volumes of this specific supplement. This 3rd supplement adds on to the previous volumes dealing with boron compounds beginning (in parentheses: literature closing dates) with the Main Volume (end of 1925), Supplement Volume 1 (end of 1949), Supplement Volume 2 (end of 1975 for boron carbides, mid-1980 for elemental boron), "Boron Compounds" Volumes 1 to 20 and Formula Index, "Boron Compounds" 1st Supplement (3 volumes, end of 1977), and "Boron Compounds" 2nd Supplement (2 volumes, through 1980). In the 3rd supplement the literature is covered uniformly through 1984.

The present volume contains the description of boron compounds with Cl, Br, and I, as well as the systems of boron with S, Se, Te, and Po. The final chapter describes the carboranes; it contains the description of carboranes as well as brief discussions of metallacarboranes and a listing of carborane-containing polymers.

The IUPAC nomenclature is mostly adhered to; occasional abbreviations for compounds are explained in the text. Unless otherwise noted, a positive sign for the chemical shifts on the NMR signals indicates downfield from the references: $(CH_3)_4Si$ for δ^1H and $\delta^{13}C$, $(C_2H_5)_2O{-}BF_3$ for $\delta^{11}B$, aqueous $NaNO_3$ for $\delta^{14}N$, and $CFCl_3$ for $\delta^{19}F$.

Lexington, Kentucky (USA)
Frankfurt am Main
July 1988

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. 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.
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"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" 2nd Suppl. Vol. 1	Boron and Noble Gases. Boron and Hydrogen. Boron and Oxygen. Boron and Nitrogen. Formula Index. Literature coverage through 1980.
"Boron Compounds" 2nd Suppl. Vol. 2	Boron and Halogens. Boron and Chalcogens. Carboranes. Formula Index. Literature coverage through 1980.
"Boron Compounds" 3rd Suppl. Vol. 1	Boron and Hydrogen Literature coverage through 1984.
"Boron Compounds" 3rd Suppl. Vol. 2	Boron and Oxygen Literature coverage through 1984.
"Boron Compounds" 3rd Suppl. Vol. 3	Boron and Nitrogen, Boron and Fluorine – 1988 Literature coverage through 1984.
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6 The System Boron-Chlorine

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Previous coverage, see "Boron Compounds" 2nd Suppl. Vol. 2, 1982, pp. 77/124.

6.1 Binary Species

6.1.1 BCl and BCl_2

BCl. Thermodynamic data obtained from a combination of tungsten transport measurements and theoretical considerations are: $\Delta H_{298} = 151$ kJ/mol; $S_{298} = 213\ J \cdot mol^{-1} \cdot K^{-1}$; $C_{p,298} = 32\ J \cdot mol \cdot K$ [1]. The bond order-dependent enthalpy term E(BCl) is obtained from the relationship $E(BCl) = A[n(BF)]^m$ to be 531.8 kJ/mol (bond order $n = 3$), and the standard heat of formation $\Delta H_f^\circ(g) = 149.5$ kJ/mol (in good agreement with the value given above) [2].

Generating BCl in a 3.7 m absorption cell by a d.c. glow discharge through BCl_3 led to observation of the pure rotational spectrum of BCl. Rotational transitions of $^{11}B^{35}Cl$ and $^{11}B^{37}Cl$ in the vibrational ground state (split into several components by nuclear electric quadrupole interactions) have been analyzed to yield molecular constants such as the nuclear quadrupole coupling constant eQq; eQq(Cl) for $^{11}B^{35}Cl = -16.737$ MHz and eQq(B) $= -3.70$ MHz (the latter datum was obtained from a line shape simulation), while eQq(Cl) for $^{11}B^{37}Cl$ was determined to be -13.191 MHz. The corrected nuclear quadrupole coupling constant (taking into account a 0.12 electron delocalization from Cl to B) is -23 MHz. For a tabulation of the observed rotational transition frequencies, additional data and a discussion of the results, see [3].

The infrared spectrum of the $\Delta v = 1$ band of BCl generated in the optical path from BCl_3 by either a microwave or a d.c. discharge has been measured with a tunable diode laser from 828 to 870 cm^{-1}. Spectra of all natural abundant species were present and the v = 1-0, 2-1, 3-2, and 4-3 transitions have been observed. The band center for v = 1-0 transition of $^{11}B^{35}Cl$ is at $\nu_0 = 829.4087\ cm^{-1}$. A set of eight Dunham coefficients was determined by fitting the data of all isotopic species with the appropriate reduced mass factors. The B–Cl distance was calculated to be r(B–Cl) = 171.52 pm and the dipole moment was estimated to be $\mu = \pm 0.1$ D [4].

The $A^1\Pi$-$X^1\Sigma^+$ transition of BCl has been analyzed up to $v'' = 9$ and $v' = 8$ in a microwave discharge through helium containing traces of BCl_3. Precise molecular constants have been obtained for the two cited electronic states. The excited $A^1\Pi$ state seems to encounter undefined perturbations. The equilibrium constants determined for $^{11}B^{35}Cl$ are compiled in Table 6/1, p. 2 [5]. For the tabulation of rotational constants, origins of the individual bands, vibrational analyses, and equilibrium constants for the less abundant isotopic species, see [5].

Table 6/1
Equilibrium Constants for $^{11}B^{35}Cl$ (in cm^{-1}; standard deviations in parentheses) [5].

	$X^1\Sigma^+$	$A^1\Pi$
B_e	0.684392(73)	0.70792(51)
a_e	0.006764(34) (calcd: 0.0061)	0.01088(58) (calcd: 0.0115)
γ_e	−0.0000277(33)	−0.00034(15)
ε_e	—	0.000077(11)
$D_3 \times 10^6$	1.919(13) (calcd: 1.82)	2.233(77) (calcd: 1.95)
$\beta_e \times 10^6$	—	−0.128(47) (calcd: −0.073)
$\delta_e \times 10^6$	—	0.0470(57)
T_e	0	36750.24
ω_e	840.01(17)	852.25(59)
$\omega_e X_e$	5.426(38)	12.91(26)
$\omega_e Y_e$	−0.0253(25)	−0.160(41)
$\omega_e Z_e$	—	0.0418(22)

The $A^1\Pi$-$X^1\Sigma^+$ transition of BCl produced by pulsed CO_2 laser irradiation from BCl_3 has also been analyzed [6]. The results presented in Table 6/2 are in fair agreement with the later ones [5]. The dissociation energy $D(BCl\,^1\Sigma^+)$ was calculated to be 5.6 eV [6]. For the application of molecular calculations in the effective potential approximation using a basis of Slater-type orbitals to BCl, see [7].

Table 6/2
Vibrational Constants for $^{11}B^{35}Cl$ and $^{10}B^{35}Cl$ (in cm^{-1}) [6].

	$X^1\Sigma^+$		$A^1\Pi$	
	$^{11}B^{35}Cl$	$^{10}B^{35}Cl$	$^{11}B^{35}Cl$	$^{10}B^{35}Cl$
ω_e	840.14 ±0.4	870.9 ±0.9	850.09 ±0.4	881.8 ±0.9
$\omega_e X_e$	5.09 ±0.27	5.22 ±0.4	10.9 ±0.2	12.3 ±0.4
$\omega_e Y_e$	−0.05 ±0.03	−0.13 ±0.09	−0.26 ±0.03	−0.14 ±0.06
$\omega_e Z_e$	−0.004 ±0.0016	−0.001 ±0.004	0.015 ±0.0016	0.025 ±0.003

The luminescence generated in BCl_3 by radiation from a pulsed CO_2 laser is due to the radiative recombination of BCl molecules with chlorine atoms. The rate constant of this reaction between 2300 and 3100 K is represented by: $k_{eff} = 4.38 \times 10^8 \exp(19300/RT)$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ [8]. BCl is an intermediate in the discharge synthesis of B_2Cl_4 and can be detected spectroscopically in the plasma from BCl_3 in the radiofrequency discharge [10].

Errors in the calculation of parameters of multi-component systems behind a shock-wave front have been evaluated using an algorithm and computer program. The system originating from BCl_3 and H_2 contains 17 components including BCl and BCl_2. For details, see [9].

BCl_2. Thermochemical data for BCl_2 obtained by a combination of tungsten transport measurements and theoretical estimates are: $\Delta H_{298} = -117$ kJ/mol, $S_{298} = 272$ $J \cdot mol^{-1} \cdot K^{-1}$, and $C_{p,298} = 46$ $J \cdot mol^{-1} \cdot K^{-1}$ [1].