

Gmelin Handbook of Inorganic Chemistry

8th Edition

B **Boron Compounds**

3rd Supplement Volume 3

Boron and Nitrogen, Boron and Fluorine

With 62 illustrations

AUTHOR

Anton Meller, Universität Göttingen, Institut für
Anorganische Chemie, Göttingen

EDITORS

Karl-Christian Buschbeck, Gmelin-Institut, Frankfurt/Main
Kurt Niedenzu, Department of Chemistry,
University of Kentucky, Lexington, Kentucky, USA

System Number 13

Table of Contents

	Page
4 The System Boron-Nitrogen	1
4.1 Binary Species	1
4.1.1 Boron Nitride, BN	1
General Remarks	1
Synthesis and Formation of Polymeric Boron Nitride	1
Hexagonal Boron Nitride with Graphite-Type Structure (α -BN) and Other Structures of Normal Density	1
Diamond-Like Boron Nitride Modifications	3
Cubic Boron Nitride with Sphalerite Structure (β -BN)	3
Boron Nitride Films with β -BN Structure	5
Hexagonal Boron Nitride with Wurtzite Structure (γ -BN) and Mixtures of Different BN Phases	6
Structural and Physical Properties	12
Hexagonal α -Boron Nitride	12
Dense Forms of Boron Nitride	14
Cubic β -Boron Nitride	14
Wurtzite-Type γ -BN	17
The Monomeric Boron Nitride Molecule	20
Energy Band Structure, Optical Properties, and Spectroscopic Phenomena of α -BN	21
Spectroscopic Properties of Boron Nitride Plasma	24
Physical Adsorption on Hexagonal Graphitic Boron Nitride (α -BN)	24
Electronic Structure and Energy Bands in Cubic (β -BN) and Wurtzite Type (γ -BN) Boron Nitride	28
Chemical Behavior of Boron Nitride	31
Hexagonal α -BN	31
Dense Forms of Boron Nitride (β -BN, cubic; γ -BN, hexagonal)	32
Analytical	33
Technical Applications of Boron Nitride	35
BN Fibers and Their Applications	35
Preparation of BN Coatings by Chemical Vapor Deposition; Similar Processes and the Application of BN Coatings	37
Metallization of Boron Nitride	39
Ceramic and Sintered Materials From or Including Boron Nitride	45
Ceramics Consisting of or Containing α -BN	45
Ceramics Consisting of or Containing the Dense Forms of BN	52
Boron Nitride as a Component of Alloys	56
α -BN Alloy Composites	56
β - and γ -BN Alloy Composites	59
Boron Nitride as Filler in Organic Polymers	66
α -BN in Resins	66
β - and γ -BN in Resins	67
Machining of Metals Using the Dense Modifications of Boron Nitride	71
Applications of Boron Nitride as a Solid Lubricant	75

	Page
Processing Applications	81
In Semiconductor and Related Uses	81
Applications Related to Laser and Nuclear Technology	82
Additional Applications	82
Boron Nitride Phases with Additional Elements	89
4.1.2 Nitrogen-Deficient Boron Nitride	91
4.2 Boron-Nitrogen Compounds Containing Hydrogen	91
4.2.1 Trisaminoborane and Its Derivatives	91
Trisaminoborane, $B(NH_2)_3$	91
Symmetrically Substituted Trisaminoboranes, $B(NRR')_3$	91
Unsymmetrically Substituted Trisaminoboranes	94
Additional Trisaminoboranes	98
4.2.2 Bisaminoboranes	100
Amino-iminoborane, $HNBNH_2$, and Its Derivatives	100
Bisaminoborane, $HB(NH_2)_2$, and Linear $(-BH-NH-)$ Polymers	100
Noncyclic Derivatives	102
Heterocycles Containing Trigonal Annular Boron	112
Species Containing One Boron Atom	112
Species Containing Two Boron Atoms	118
Heterocycles Containing Four-Coordinate Boron	121
4.2.3 Borazine and Derivatives Thereof	126
Borazine, $(-BH-NH-)_3$	126
B-Trihydroborazines, $(-BH-NR-)_3$	129
N-Trihydroborazines, $(-BR-NH-)_3$	130
N-Triorganylborazines	130
B-Triorganyl-N-Triorganylborazines, $(-BR-NR-)_3$	130
Unsymmetrically Substituted Borazines	133
Oligomers and Polymers	133
4.2.4 Additional Boron-Nitrogen Heterocycles	134
1-Aza-2,3-diborirines and 1,2-Diaza-3-borirines	134
1,3,2,4-Diazadiboretidines	135
Derivatives of Octahydro-1,3,5,7-tetraaza-2,4,6,8-tetraborocine	136
Derivatives of 1,2,4,3,5-Triazadiboroline	137
Derivatives of 2-Tetraazaboroline	137
Additional Cyclic Compounds with a B-N Skeleton	138
4.2.5 Boron-Nitrogen Heterocycles Containing Additional Heteroatoms Other Than Carbon	139
4.2.6 Iminoborane, $HN=BH$, and Related Species	141
4.2.7 Pseudohaloboranes Containing One B-N Bond	144

	Page
4.2.8 Monoaminoborane and Its Derivatives	145
(Amino)hydroboranes	145
(Amino)organylboranes and Related Species	147
Aminoboranes Containing More Than One Boron Atom	159
Organoboron-Nitrogen Heterocycles of the Monoaminoborane Type	162
4.2.9 Ammine-Borane and Its Derivatives	168
Dinitrogen-Borane	168
Ammine-Borane and Adducts of the Types $L-BH_3$ and $L(BH_3)_n$	168
Adducts of the Types $L-BH_2X$, $L-BH_2R$, and $L-BR_2R'$	184
4.2.10 Pyrazaboles and Related Compounds	194
Pyrazolylboranes and Pyrazaboles	194
Poly(pyrazolyl-1-yl)borates	202
4.2.11 Nitrogen-Substituted Boron Cations with Coordination Numbers Two to Four	203
Two-Coordinate Boron Cations	203
Three-Coordinate Boron Cations	206
Four-Coordinate Boron Cations	210
4.2.12 Aminoborate Ions and Related Species	211
Aminoborate Ions	211
Isocyanohydroborates(1-)	212
Amino-Cyanoborates(1-)	213
Additional Aminoborates(1-)	213
Aminoborates(2-)	214
Aminoborates(3-)	214
Five-Coordinate and Six-Coordinate Aminoborate Anions	214
4.3 Boron-Nitrogen Compounds Containing Oxygen	216
4.3.1 Noncyclic Species	216
4.3.2 Cyclic Species	217
4.3.3 Ammonium Borates	225
Preparation and Physical Properties	225
Applications	227
5 The System Boron-Fluorine	231
5.1 Binary Species	231
5.1.1 The BF Molecule and the BF^+ Ion	231
5.1.2 The BF_2 Radical and the BF_2^+ Ion	235
5.1.3 Trifluoroborane, BF_3	239

	Page
Preparation, Purification, and Recovery of BF_3 and Its Use for Chemical Separation of Boron Isotopes	239
Structure Determinations	240
Thermochemical Data	242
Photoelectron Spectroscopic, X-Ray Photoelectron Spectroscopic, and Related Theoretical Studies	242
Nuclear Magnetic Resonance Data	245
Vibrational-Rotational Spectroscopy	246
Additional Physicochemical Data	248
Chemical Behavior and Applications	251
General Aspects and Interactions with Inorganic Materials	251
Interaction with Organic Materials	252
Catalytic Applications of BF_3	254
Application in Polymerization and Condensation Reactions	259
Miscellaneous Uses of BF_3	263
BF_3 as a Dopant	263
Nuclear Applications of BF_3	264
Various Technical Applications	264
Analytical Determinations	264
Adducts of BF_3 with Oxygen Donor Molecules	267
The Adduct $(\text{C}_2\text{H}_5)_2\text{O}-\text{BF}_3$	267
Additional Species	285
Complexes of BF_3 with Nitrogen Donor Molecules	292
Additional Complexes of BF_3 with Donor Molecules	295
5.1.4 Tetrafluoroborates	301
General Data of $[\text{BF}_4]^-$	301
Application of Tetrafluoroborates. Analytical Methods. Removal	303
Tetrafluoroboric Acid, $\text{H}[\text{BF}_4]$	307
Alkali Metal Tetrafluoroborates	318
$\text{Li}[\text{BF}_4]$	318
$\text{Na}[\text{BF}_4]$	322
$\text{K}[\text{BF}_4]$, $\text{Rb}[\text{BF}_4]$, $\text{Cs}[\text{BF}_4]$	326
Trialkyloxonium Tetrafluoroborates, $[\text{R}_3\text{O}][\text{BF}_4]$, and Acetyl Tetrafluoroborate, $[\text{CH}_3\text{CO}][\text{BF}_4]$	334
Ammonium Tetrafluoroborate, $[\text{NH}_4][\text{BF}_4]$	340
Alkylammonium Tetrafluoroborates, $[\text{NH}_{4-x}\text{R}_x][\text{BF}_4]$	343
Tetrafluoroammonium Tetrafluoroborate, $[\text{NF}_4][\text{BF}_4]$	345
Nitrosonium Tetrafluoroborate, $[\text{NO}][\text{BF}_4]$	350
Nitronium Tetrafluoroborate, $[\text{NO}_2][\text{BF}_4]$	353
Additional Tetrafluoroborates	354
5.2 Compounds Containing Hydrogen	359
5.2.1 The Species HBF_2 and H_2BF	359
5.2.2 Ionic Species	361

	Page
5.2.3 (Organyl)fluoroboranes	362
(Organyl)difluoroboranes, RBF_2^-	362
(Diorganyl)fluoroboranes, R_2BF	363
5.3 Compounds Containing Oxygen	365
Cyclic Compounds Containing Tetracoordinate $[\text{O}_2\text{BF}_2]$ Groups	367
5.4 Compounds Containing Nitrogen	375
5.4.1 (Amino)fluoroboranes	375
5.4.2 Cyclic Species	376
With Three-Coordinate Boron	376
Species with Four-Coordinate Boron	377
5.4.3 Compounds with Nitrogen and Oxygen	378
5.4.4 Cyanofluoroborates and Additional Ionic Species	378
Table of Conversion Factors	381