

# Inorganic Chemistry

---

**Third Edition**

**GARY L. MIESSLER ■ DONALD A. TARR**

St. Olaf College  
Northfield, Minnesota



Pearson Education International

---

# Brief Contents

---

Preface	xiii
<b>1</b>	Introduction to Inorganic Chemistry 1
<b>2</b>	Atomic Structure 15
<b>3</b>	Simple Bonding Theory 51
<b>4</b>	Symmetry and Group Theory 76
<b>5</b>	Molecular Orbitals 116
<b>6</b>	Acid-Base and Donor-Acceptor Chemistry 165
<b>7</b>	The Crystalline Solid State 207
<b>8</b>	Chemistry of the Main Group Elements 240
<b>9</b>	Coordination Chemistry I: Structures and Isomers 299
<b>10</b>	Coordination Chemistry II: Bonding 337
<b>11</b>	Coordination Chemistry III: Electronic Spectra 379
<b>12</b>	Coordination Chemistry IV: Reactions and Mechanisms 412
<b>13</b>	Organometallic Chemistry 454
<b>14</b>	Organometallic Reactions and Catalysis 520
<b>15</b>	Parallels Between Main Group and Organometallic Chemistry 556
<b>16</b>	Bioinorganic and Environmental Chemistry 594
<b>Appendix A</b>	Answers to Exercises 637
<b>Appendix B-1</b>	Ionic Radii 668
<b>Appendix B-2</b>	Ionization Energy 671
<b>Appendix B-3</b>	Electron Affinity 672
<b>Appendix B-4</b>	Electronegativity 673
<b>Appendix B-5</b>	Absolute Hardness Parameters 674
<b>Appendix B-6</b>	$C_A$ , $E_A$ , $C_B$ , and $E_B$ Values 675
<b>Appendix B-7</b>	Latimer Diagrams for Selected Elements 676
<b>Appendix C</b>	Character Tables 681
<b>Appendix D</b>	Electron-Dot Diagrams and Formal Charge 691
	Index 697

# Contents

---

## PREFACE    xiii

### 1 INTRODUCTION TO INORGANIC CHEMISTRY 1

- 1-1 What is Inorganic Chemistry? 1
- 1-2 Contrasts with Organic Chemistry 1
- 1-3 Genesis of the Elements (The Big Bang) and Formation of the Earth 5
- 1-4 Nuclear Reactions and Radioactivity 8
- 1-5 Distribution of Elements on Earth 9
- 1-6 The History of Inorganic Chemistry 11

### 2 ATOMIC STRUCTURE 15

- 2-1 Historical Development of Atomic Theory 15
  - 2-1-1 *The Periodic Table* 16
  - 2-1-2 *Discovery of Subatomic Particles and the Bohr Atom* 17
- 2-2 The Schrödinger Equation 21
  - 2-2-1 *The Particle in a Box* 23
  - 2-2-2 *Quantum Numbers and Atomic Wave Functions* 25
  - 2-2-3 *The Aufbau Principle* 34
  - 2-2-4 *Shielding* 38
- 2-3 Periodic Properties of Atoms 43
  - 2-3-1 *Ionization Energy* 43
  - 2-3-2 *Electron Affinity* 44
  - 2-3-3 *Covalent and Ionic Radii* 44

### 3 SIMPLE BONDING THEORY 51

- 3-1 Lewis Electron-Dot Diagrams 51
  - 3-1-1 *Resonance* 52
  - 3-1-2 *Expanded Shells* 53
  - 3-1-3 *Formal Charge* 53
  - 3-1-4 *Multiple Bonds in Be and B Compounds* 56
- 3-2 Valence Shell Electron Pair Repulsion Theory 57
  - 3-2-1 *Lone Pair Repulsion* 59
  - 3-2-2 *Multiple Bonds* 62
  - 3-2-3 *Electronegativity and Atomic Size Effects* 63
  - 3-2-4 *Ligand Close-Packing* 66
- 3-3 Polar Molecules 67
- 3-4 Hydrogen Bonding 69

## **4 SYMMETRY AND GROUP THEORY 76**

- 4-1 Symmetry Elements and Operations 76
- 4-2 Point Groups 82
  - 4-2-1 *Groups of Low and High Symmetry* 84
  - 4-2-2 *Other Groups* 86
- 4-3 Properties and Representations of Groups 92
  - 4-3-1 *Matrices* 92
  - 4-3-2 *Representations of Point Groups* 94
  - 4-3-3 *Character Tables* 97
- 4-4 Examples and Applications of Symmetry 102
  - 4-4-1 *Chirality* 102
  - 4-4-2 *Molecular Vibrations* 103

## **5 MOLECULAR ORBITALS 116**

- 5-1 Formation of Molecular Orbitals from Atomic Orbitals 116
  - 5-1-1 *Molecular Orbitals from s Orbitals* 117
  - 5-1-2 *Molecular Orbitals from p Orbitals* 119
  - 5-1-3 *Molecular Orbitals from d Orbitals* 120
  - 5-1-4 *Nonbonding Orbitals and Other Factors* 122
- 5-2 Homonuclear Diatomic Molecules 122
  - 5-2-1 *Molecular Orbitals* 122
  - 5-2-2 *Orbital Mixing* 124
  - 5-2-3 *First and Second Row Molecules* 125
  - 5-2-4 *Photoelectron Spectroscopy* 130
  - 5-2-5 *Correlation Diagrams* 132
- 5-3 Heteronuclear Diatomic Molecules 134
  - 5-3-1 *Polar Bonds* 134
  - 5-3-2 *Ionic Compounds and Molecular Orbitals* 138
- 5-4 Molecular Orbitals for Larger Molecules 139
  - 5-4-1  $\text{HF}^-$  140
  - 5-4-2  $\text{CO}_2$  143
  - 5-4-3  $\text{H}_2\text{O}$  148
  - 5-4-4  $\text{NH}_3$  151
  - 5-4-5  $\text{BF}_3$  154
  - 5-4-6 *Molecular Shapes* 157
  - 5-4-7 *Hybrid Orbitals* 157
- 5-5 Expanded Shells and Molecular Orbitals 161

## **6 ACID-BASE AND DONOR-ACCEPTOR CHEMISTRY 165**

- 6-1 Acid-Base Concepts as Organizing Concepts 165
  - 6-1-1 *History* 165
- 6-2 Major Acid-Base Concepts 166
  - 6-2-1 *Arrhenius Concept* 166
  - 6-2-2 *Brønsted-Lowry Concept* 167
  - 6-2-3 *Solvent System Concept* 168
  - 6-2-4 *Lewis Concept* 170
  - 6-2-5 *Frontier Orbitals and Acid-Base Reactions* 171
  - 6-2-6 *Hydrogen Bonding* 174
  - 6-2-7 *Electronic Spectra (Including Charge Transfer)* 178

6-3	Hard and Soft Acids and Bases	179
6-3-1	<i>Theory of Hard and Soft Acids and Bases</i>	183
6-3-2	<i>Quantitative Measures</i>	187
6-4	Acid and Base Strength	192
6-4-1	<i>Measurement of Acid-Base Interactions</i>	192
6-4-2	<i>Thermodynamic Measurements</i>	193
6-4-3	<i>Proton Affinity</i>	194
6-4-4	<i>Acidity and Basicity of Binary Hydrogen Compounds</i>	194
6-4-5	<i>Inductive Effects</i>	196
6-4-6	<i>Strength of Oxyacids</i>	196
6-4-7	<i>Acidity of Cations in Aqueous Solution</i>	197
6-4-8	<i>Steric Effects</i>	199
6-4-9	<i>Solvation and Acid-Base Strength</i>	200
6-4-10	<i>Nonaqueous Solvents and Acid-Base Strength</i>	201
6-4-11	<i>Superacids</i>	203

## 7 THE CRYSTALLINE SOLID STATE 207

7-1	Formulas and Structures	207
7-1-1	<i>Simple Structures</i>	207
7-1-2	<i>Structures of Binary Compounds</i>	214
7-1-3	<i>More Complex Compounds</i>	218
7-1-4	<i>Radius Ratio</i>	218
7-2	Thermodynamics of Ionic Crystal Formation	220
7-2-1	<i>Lattice Energy and Madelung Constant</i>	220
7-2-2	<i>Solubility, Ion Size (Large-Large and Small-Small), and HSAB</i>	222
7-3	Molecular Orbitals and Band Structure	223
7-3-1	<i>Diodes, The Photovoltaic Effect, and Light-Emitting Diodes</i>	226
7-4	Superconductivity	228
7-4-1	<i>Low-Temperature Superconducting Alloys</i>	228
7-4-2	<i>The Theory of Superconductivity (Cooper Pairs)</i>	229
7-4-3	<i>High-Temperature Superconductors (YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> and Related Compounds)</i>	230
7-5	Bonding in Ionic Crystals	231
7-6	Imperfections in Solids	231
7-7	Silicates	232

## 8 CHEMISTRY OF THE MAIN GROUP ELEMENTS 240

8-1	General Trends in Main Group Chemistry	241
8-1-1	<i>Physical Properties</i>	241
8-1-2	<i>Electronegativity</i>	243
8-1-3	<i>Ionization Energy</i>	244
8-1-4	<i>Chemical Properties</i>	244
8-2	Hydrogen	247
8-2-1	<i>Chemical Properties</i>	248
8-3	Group 1 (IA): The Alkali Metals	249
8-3-1	<i>The Elements</i>	249
8-3-2	<i>Chemical Properties</i>	250
8-4	Group 2 (IIA): The Alkaline Earths	253
8-4-1	<i>The Elements</i>	253
8-4-2	<i>Chemical Properties</i>	254

8-5	Group 13 (IIIA)	256
8-5-1	<i>The Elements</i>	256
8-5-2	<i>Other Chemistry of the Group 13 (IIIA) Elements</i>	260
8-6	Group 14 (IVA)	261
8-6-1	<i>The Elements</i>	261
8-6-2	<i>Compounds</i>	267
8-7	Group 15 (VA)	272
8-7-1	<i>The Elements</i>	272
8-7-2	<i>Compounds</i>	274
8-8	Group 16 (VIA)	279
8-8-1	<i>The Elements</i>	279
8-9	Group 17 (VIIA): The Halogens	285
8-9-1	<i>The Elements</i>	285
8-10	Group 18 (VIIIA): The Noble Gases	291
8-10-1	<i>The Elements</i>	291
8-10-2	<i>Chemistry</i>	292

## 9 COORDINATION CHEMISTRY I: STRUCTURES AND ISOMERS 299

9-1	History	299
9-2	Nomenclature	304
9-3	Isomerism	309
9-3-1	<i>Stereoisomers</i>	310
9-3-2	<i>Four-Coordinate Complexes</i>	310
9-3-3	<i>Chirality</i>	311
9-3-4	<i>Six-Coordinate Complexes</i>	311
9-3-5	<i>Combinations of Chelate Rings</i>	315
9-3-6	<i>Ligand Ring Conformation</i>	318
9-3-7	<i>Constitutional Isomers</i>	319
9-3-8	<i>Experimental Separation and Identification of Isomers</i>	322
9-4	Coordination Numbers and Structures	323
9-4-1	<i>Low Coordination Numbers (CN = 1, 2, and 3)</i>	325
9-4-2	<i>Coordination Number 4</i>	327
9-4-3	<i>Coordination Number 5</i>	328
9-4-4	<i>Coordination Number 6</i>	329
9-4-5	<i>Coordination Number 7</i>	331
9-4-6	<i>Coordination Number 8</i>	332
9-4-7	<i>Larger Coordination Numbers</i>	333

## 10 COORDINATION CHEMISTRY II: BONDING 337

10-1	Experimental Evidence for Electronic Structures	337
10-1-1	<i>Thermodynamic Data</i>	337
10-1-2	<i>Magnetic Susceptibility</i>	339
10-1-3	<i>Electronic Spectra</i>	342
10-1-4	<i>Coordination Numbers and Molecular Shapes</i>	342
10-2	Theories of Electronic Structure	342
10-2-1	<i>Terminology</i>	342
10-2-2	<i>Historical Background</i>	343
10-3	Ligand Field Theory	345
10-3-1	<i>Molecular Orbitals for Octahedral Complexes</i>	345
10-3-2	<i>Orbital Splitting and Electron Spin</i>	346
10-3-3	<i>Ligand Field Stabilization Energy</i>	350

10-3-4	<i>Pi Bonding</i>	352
10-3-5	<i>Square-Planar Complexes</i>	356
10-3-6	<i>Tetrahedral Complexes</i>	360
10-4	<i>Angular Overlap</i>	362
10-4-1	<i>Sigma-Donor Interactions</i>	362
10-4-2	<i>Pi-Acceptor Interactions</i>	364
10-4-3	<i>Pi-Donor Interactions</i>	366
10-4-4	<i>Types of Ligands and the Spectrochemical Series</i>	367
10-4-5	<i>Magnitudes of <math>e_g</math>, <math>e_\pi</math>, and <math>\Delta</math></i>	368
10-5	<i>The Jahn-Teller Effect</i>	370
10-6	<i>Four- and Six-Coordinate Preferences</i>	373
10-7	<i>Other Shapes</i>	375

## 11 COORDINATION CHEMISTRY III: ELECTRONIC SPECTRA 379

11-1	<i>Absorption of Light</i>	380
11-1-1	<i>Beer-Lambert Absorption Law</i>	380
11-2	<i>Quantum Numbers of Multielectron Atoms</i>	382
11-2-1	<i>Spin-Orbit Coupling</i>	387
11-3	<i>Electronic Spectra of Coordination Compounds</i>	388
11-3-1	<i>Selection Rules</i>	390
11-3-2	<i>Correlation Diagrams</i>	391
11-3-3	<i>Tanabe-Sugano Diagrams</i>	393
11-3-4	<i>Jahn-Teller Distortions and Spectra</i>	398
11-3-5	<i>Examples of Applications of Tanabe-Sugano Diagrams: Determining <math>\Delta_0</math> from Spectra</i>	401
11-3-6	<i>Tetrahedral Complexes</i>	406
11-3-7	<i>Charge-Transfer Spectra</i>	407

## 12 COORDINATION CHEMISTRY IV: REACTIONS AND MECHANISMS 412

12-1	<i>History and Principles</i>	412
12-2	<i>Substitution Reactions</i>	414
12-2-1	<i>Inert and Labile Compounds</i>	414
12-2-2	<i>Mechanisms of Substitution</i>	415
12-3	<i>Kinetic Consequences of Reaction Pathways</i>	417
12-3-1	<i>Dissociation (D)</i>	417
12-3-2	<i>Interchange (I)</i>	418
12-3-3	<i>Association (A)</i>	419
12-4	<i>Experimental Evidence in Octahedral Substitution</i>	420
12-4-1	<i>Dissociation</i>	420
12-4-2	<i>Linear Free Energy Relationships</i>	423
12-4-3	<i>Associative Mechanisms</i>	425
12-4-4	<i>The Conjugate Base Mechanism</i>	426
12-4-5	<i>The Kinetic Chelate Effect</i>	428
12-5	<i>Stereochemistry of Reactions</i>	429
12-5-1	<i>Substitution in trans Complexes</i>	430
12-5-2	<i>Substitution in cis Complexes</i>	432
12-5-3	<i>Isomerization of Chelate Rings</i>	433
12-6	<i>Substitution Reactions of Square-Planar Complexes</i>	434
12-6-1	<i>Kinetics and Stereochemistry of Square-Planar Substitutions</i>	434
12-6-2	<i>Evidence for Associative Reactions</i>	435

12-7	The <i>trans</i> Effect	437
12-7-1	<i>Explanations of the trans Effect</i>	439
12-8	Oxidation-Reduction Reactions	440
12-8-1	<i>Inner- and Outer-Sphere Reactions</i>	441
12-8-2	<i>Conditions for High and Low Oxidation Numbers</i>	445
12-9	Reactions of Coordinated Ligands	446
12-9-1	<i>Hydrolysis of Esters, Amides, and Peptides</i>	446
12-9-2	<i>Template Reactions</i>	448
12-9-3	<i>Electrophilic Substitution</i>	449

## **13 ORGANOMETALLIC CHEMISTRY 454**

13-1	Historical Background	457
13-2	Organic Ligands and Nomenclature	458
13-3	The 18-Electron Rule	460
13-3-1	<i>Counting Electrons</i>	460
13-3-2	<i>Why 18 Electrons?</i>	463
13-3-3	<i>Square-Planar Complexes</i>	465
13-4	Ligands in Organometallic Chemistry	467
13-4-1	<i>Carbonyl (CO) Complexes</i>	467
13-4-2	<i>Ligands Similar to CO</i>	475
13-4-3	<i>Hydride and Dihydrogen Complexes</i>	477
13-4-4	<i>Ligands Having Extended <math>\pi</math> Systems</i>	479
13-5	Bonding Between Metal Atoms and Organic $\Pi$ Systems	482
13-5-1	<i>Linear <math>\pi</math> Systems</i>	482
13-5-2	<i>Cyclic <math>\pi</math> Systems</i>	485
13-5-3	<i>Fullerene Complexes</i>	492
13-6	Complexes Containing M—C, M=C, and M≡C Bonds	496
13-6-1	<i>Alkyl and Related Complexes</i>	496
13-6-2	<i>Carbene Complexes</i>	498
13-6-3	<i>Carbyne (Alkyldyne) Complexes</i>	501
13-7	Spectral Analysis and Characterization of Organometallic Complexes	503
13-7-1	<i>Infrared Spectra</i>	503
13-7-2	<i>NMR Spectra</i>	507
13-7-3	<i>Examples of Characterization</i>	509

## **14 ORGANOMETALLIC REACTIONS AND CATALYSIS 520**

14-1	Reactions Involving Gain or Loss of Ligands	520
14-1-1	<i>Ligand Dissociation and Substitution</i>	521
14-1-2	<i>Oxidative Addition</i>	524
14-1-3	<i>Reductive Elimination</i>	525
14-1-4	<i>Nucleophilic Displacement</i>	526
14-2	Reactions Involving Modification of Ligands	528
14-2-1	<i>Insertion</i>	528
14-2-2	<i>Carbonyl Insertion (Alkyl Migration)</i>	528
14-2-3	<i>1,2 Insertions</i>	533
14-2-4	<i>Hydride Elimination</i>	533
14-2-5	<i>Abstraction</i>	534
14-3	Organometallic Catalysts	534
14-3-1	<i>Example of Catalysis: Catalytic Deuteration</i>	535
14-3-2	<i>Hydroformylation</i>	535
14-3-3	<i>Monsanto Acetic Acid Process</i>	538
14-3-4	<i>Wacker (Smidt) Process</i>	541
14-3-5	<i>Hydrogenation by Wilkinson's Catalyst</i>	542

14-3-6	<i>Olefin Metathesis</i>	544
14-4	Heterogeneous Catalysts	548
14-4-1	<i>Ziegler-Natta Polymerizations</i>	548
14-4-2	<i>Water Gas Reaction</i>	549

## 15 PARALLELS BETWEEN MAIN GROUP AND ORGANOMETALLIC CHEMISTRY 556

15-1	Main Group Parallels with Binary Carbonyl Complexes	556
15-2	The Isobal Analogy	558
15-2-1	<i>Extensions of the Analogy</i>	561
15-2-2	<i>Examples of Applications of the Analogy</i>	565
15-3	Metal-Metal Bonds	566
15-3-1	<i>Multiple Metal-Metal Bonds</i>	568
15-4	Cluster Compounds	572
15-4-1	<i>Boranes</i>	572
15-4-2	<i>Heteroboranes</i>	577
15-4-3	<i>Metallaboranes and Metallacarboranes</i>	579
15-4-4	<i>Carbonyl Clusters</i>	582
15-4-5	<i>Carbide Clusters</i>	587
15-4-6	<i>Additional Comments on Clusters</i>	588

## 16 BIOINORGANIC AND ENVIRONMENTAL CHEMISTRY 594

16-1	Porphyrins and Related Complexes	596
16-1-1	<i>Iron Porphyrins</i>	597
16-1-2	<i>Similar Ring Compounds</i>	600
16-2	Other Iron Compounds	604
16-3	Zinc and Copper Enzymes	606
16-4	Nitrogen Fixation	611
16-5	Nitric Oxide	616
16-6	Inorganic Medicinal Compounds	618
16-6-1	<i>Cisplatin and Related Complexes</i>	618
16-6-2	<i>Auranofin and Arthritis Treatment</i>	622
16-6-3	<i>Vanadium Complexes in Medicine</i>	622
16-7	Study of DNA Using Inorganic Agents	622
16-8	Environmental Chemistry	624
16-8-1	<i>Metals</i>	624
16-8-2	<i>Nonmetals</i>	629

## APPENDIX A ANSWERS TO EXERCISES 637

APPENDIX B-1	IONIC RADII	668
APPENDIX B-2	IONIZATION ENERGY	671
APPENDIX B-3	ELECTRON AFFINITY	672
APPENDIX B-4	ELECTRONEGATIVITY	673
APPENDIX B-5	ABSOLUTE HARDNESS PARAMETERS	674
APPENDIX B-6	$C_A$ , $E_A$ , $C_B$ , AND $E_B$ VALUES	675
APPENDIX B-7	LATIMER DIAGRAMS FOR SELECTED ELEMENTS	676
APPENDIX C	CHARACTER TABLES	681
APPENDIX D	ELECTRON-DOT DIAGRAMS AND FORMAL CHARGE	691

## INDEX 697