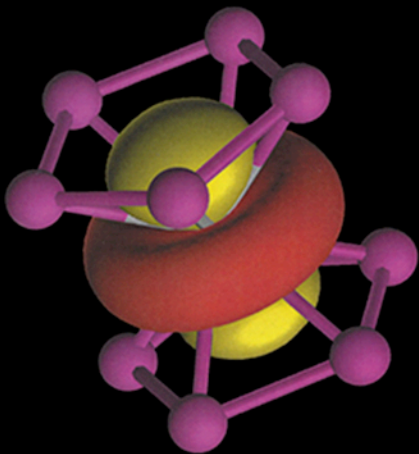


Fifth Edition

Inorganic Chemistry



Gary L. Miessler,
Paul J. Fischer, and Donald A. Tarr

FIFTH EDITION

Inorganic Chemistry

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Brief Contents

Chapter 1	Introduction to Inorganic Chemistry	1
Chapter 2	Atomic Structure	9
Chapter 3	Simple Bonding Theory	45
Chapter 4	Symmetry and Group Theory	75
Chapter 5	Molecular Orbitals	117
Chapter 6	Acid–Base and Donor–Acceptor Chemistry	169
Chapter 7	The Crystalline Solid State	215
Chapter 8	Chemistry of the Main Group Elements	249
Chapter 9	Coordination Chemistry I: Structures and Isomers	313
Chapter 10	Coordination Chemistry II: Bonding	357
Chapter 11	Coordination Chemistry III: Electronic Spectra	403
Chapter 12	Coordination Chemistry IV: Reactions and Mechanisms	437
Chapter 13	Organometallic Chemistry	475
Chapter 14	Organometallic Reactions and Catalysis	541
Chapter 15	Parallels between Main Group and Organometallic Chemistry	579
Appendix A	Answers to Exercises	619
Appendix B	Useful Data	
App. B can be found online at www.pearsonhighered.com/advchemistry		
Appendix C	Character Tables	658

Contents

Preface xi
Acknowledgments xiii

Chapter 1

Introduction to Inorganic Chemistry 1

- 1.1 What Is Inorganic Chemistry? 1
 - 1.2 Contrasts with Organic Chemistry 1
 - 1.3 The History of Inorganic Chemistry 4
 - 1.4 Perspective 7
- General References 8*

Chapter 2

Atomic Structure 9

- 2.1 Historical Development of Atomic Theory 9
 - 2.1.1 The Periodic Table 10
 - 2.1.2 Discovery of Subatomic Particles and the Bohr Atom 11
- 2.2 The Schrödinger Equation 14
 - 2.2.1 The Particle in a Box 16
 - 2.2.2 Quantum Numbers and Atomic Wave Functions 18
 - 2.2.3 The Aufbau Principle 26
 - 2.2.4 Shielding 30
- 2.3 Periodic Properties of Atoms 36
 - 2.3.1 Ionization Energy 36
 - 2.3.2 Electron Affinity 37
 - 2.3.3 Covalent and Ionic Radii 38

General References 41 • Problems 41

Chapter 3

Simple Bonding Theory 45

- 3.1 Lewis Electron-Dot Diagrams 45
 - 3.1.1 Resonance 46
 - 3.1.2 Higher Electron Counts 46
 - 3.1.3 Formal Charge 47
 - 3.1.4 Multiple Bonds in Be and B Compounds 49
- 3.2 Valence Shell Electron-Pair Repulsion 51
 - 3.2.1 Lone-Pair Repulsion 53
 - 3.2.2 Multiple Bonds 55
 - 3.2.3 Electronegativity and Atomic Size Effects 57
 - 3.2.4 Ligand Close Packing 63
- 3.3 Molecular Polarity 66
- 3.4 Hydrogen Bonding 67

General References 70 • Problems 71

Chapter 4

Symmetry and Group Theory 75

- 4.1 Symmetry Elements and Operations 75
- 4.2 Point Groups 80
 - 4.2.1 Groups of Low and High Symmetry 82
 - 4.2.2 Other Groups 84
- 4.3 Properties and Representations of Groups 90
 - 4.3.1 Matrices 91
 - 4.3.2 Representations of Point Groups 92
 - 4.3.3 Character Tables 95

4.4 Examples and Applications of Symmetry 100

4.4.1 Chirality 100

4.4.2 Molecular Vibrations 101

General References 111 • Problems 111

Chapter 5

Molecular Orbitals 117

5.1 Formation of Molecular Orbitals from Atomic Orbitals 117

5.1.1 Molecular Orbitals from *s* Orbitals 1185.1.2 Molecular Orbitals from *p* Orbitals 1205.1.3 Molecular Orbitals from *d* Orbitals 121

5.1.4 Nonbonding Orbitals and Other Factors 122

5.2 Homonuclear Diatomic Molecules 122

5.2.1 Molecular Orbitals 123

5.2.2 Orbital Mixing 124

5.2.3 Diatomic Molecules of the First and Second Periods 126

5.2.4 Photoelectron Spectroscopy 130

5.3 Heteronuclear Diatomic Molecules 133

5.3.1 Polar Bonds 133

5.3.2 Ionic Compounds and Molecular Orbitals 138

5.4 Molecular Orbitals for Larger Molecules 140

5.4.1 FHF⁻ 1405.4.2 CO₂ 1435.4.3 H₂O 1495.4.4 NH₃ 1525.4.5 CO₂ Revisited with Projection Operators 1555.4.6 BF₃ 158

5.4.7 Hybrid Orbitals 161

General References 165 • Problems 165

Chapter 6

Acid–Base and Donor–Acceptor Chemistry 169

6.1 Acid–Base Models as Organizing Concepts 169

6.1.1 History of Acid–Base Models 169

6.2 Arrhenius Concept 170

6.3 Brønsted–Lowry Concept 171

6.3.1 Nonaqueous Solvents and Acid–Base Strength 172

6.3.2 Brønsted–Lowry Superacids 173

6.3.3 Thermodynamic Measurements in Solution 175

6.3.4 Brønsted–Lowry Gas Phase Acidity and Basicity 176

6.3.5 Brønsted–Lowry Superbases 178

6.3.6 Trends in Brønsted–Lowry Basicity 179

6.3.7 Brønsted–Lowry Acid Strength of Binary Hydrogen Compounds 182

6.3.8 Brønsted–Lowry Strength of Oxyacids 183

6.3.9 Brønsted–Lowry Acidity of Aqueous Cations 183

6.4 Lewis Acid–Base Concept and Frontier Orbitals 184

6.4.1 Frontier Orbitals and Acid–Base Reactions 185

6.4.2 Spectroscopic Support for Frontier Orbital Interactions 188

6.4.3 Quantification of Lewis Basicity 189

6.4.4 The BF₃ Affinity Scale for Lewis Basicity 191

6.4.5 Halogen Bonds 192

6.4.6 Inductive Effects on Lewis Acidity and Basicity 193

6.4.7 Steric Effects on Lewis Acidity and Basicity 194

6.4.8 Frustrated Lewis Pairs 196

6.5 Intermolecular Forces 197

6.5.1 Hydrogen Bonding 197

6.5.2 Receptor–Guest Interactions 200

6.6 Hard and Soft Acids and Bases	201	
6.6.1 Theory of Hard and Soft Acids and Bases	203	
6.6.2 HSAB Quantitative Measures	205	
<i>General References</i>	211 • <i>Problems</i>	211

Chapter 7

The Crystalline Solid State 215

7.1 Formulas and Structures	215	
7.1.1 Simple Structures	215	
7.1.2 Structures of Binary Compounds	221	
7.1.3 More Complex Compounds	224	
7.1.4 Radius Ratio	224	
7.2 Thermodynamics of Ionic Crystal Formation	226	
7.2.1 Lattice Energy and the Madelung Constant	226	
7.2.2 Solubility, Ion Size, and HSAB	227	
7.3 Molecular Orbitals and Band Structure	229	
7.3.1 Diodes, the Photovoltaic Effect, and Light-Emitting Diodes	233	
7.3.2 Quantum Dots	235	
7.4 Superconductivity	236	
7.4.1 Low-Temperature Superconducting Alloys	237	
7.4.2 The Theory of Superconductivity (Cooper Pairs)	237	
7.4.3 High-Temperature Superconductors: $\text{YBa}_2\text{Cu}_3\text{O}_7$ and Related Compounds	238	
7.5 Bonding in Ionic Crystals	239	
7.6 Imperfections in Solids	240	
7.7 Silicates	241	
<i>General References</i>	246 • <i>Problems</i>	247

Chapter 8

Chemistry of the Main Group Elements 249

8.1 General Trends in Main Group Chemistry	249
8.1.1 Physical Properties	249
8.1.2 Electronegativity	251
8.1.3 Ionization Energy	252
8.1.4 Chemical Properties	253
8.2 Hydrogen	257
8.2.1 Chemical Properties	258
8.3 Group 1: The Alkali Metals	259
8.3.1 The Elements	259
8.3.2 Chemical Properties	259
8.4 Group 2: The Alkaline Earths	262
8.4.1 The Elements	262
8.4.2 Chemical Properties	263
8.5 Group 13	265
8.5.1 The Elements	265
8.5.2 Other Chemistry of the Group 13 Elements	269
8.6 Group 14	271
8.6.1 The Elements	271
8.6.2 Compounds	280
8.7 Group 15	284
8.7.1 The Elements	285
8.7.2 Compounds	287
8.8 Group 16	290
8.8.1 The Elements	290
8.9 Group 17: The Halogens	296
8.9.1 The Elements	296

- 8.10 Group 18: The Noble Gases 300
 - 8.10.1 The Elements 300
 - 8.10.2 Chemistry of Group 18 Elements 302

General References 309 • *Problems* 309

Chapter 9

Coordination Chemistry I: Structures and Isomers 313

- 9.1 History 313
- 9.2 Nomenclature 317
- 9.3 Isomerism 322
 - 9.3.1 Stereoisomers 322
 - 9.3.2 4-Coordinate Complexes 322
 - 9.3.3 Chirality 323
 - 9.3.4 6-Coordinate Complexes 323
 - 9.3.5 Combinations of Chelate Rings 327
 - 9.3.6 Ligand Ring Conformation 329
 - 9.3.7 Constitutional Isomers 331
 - 9.3.8 Separation and Identification of Isomers 334

9.4 Coordination Numbers and Structures 336

- 9.4.1 Coordination Numbers 1, 2, and 3 337
- 9.4.2 Coordination Number 4 339
- 9.4.3 Coordination Number 5 341
- 9.4.4 Coordination Number 6 342
- 9.4.5 Coordination Number 7 343
- 9.4.6 Coordination Number 8 344
- 9.4.7 Larger Coordination Numbers 346

9.5 Coordination Frameworks 347

General References 353 • *Problems* 353

Chapter 10

Coordination Chemistry II: Bonding 357

- 10.1 Evidence for Electronic Structures 357
 - 10.1.1 Thermodynamic Data 357
 - 10.1.2 Magnetic Susceptibility 359
 - 10.1.3 Electronic Spectra 362
 - 10.1.4 Coordination Numbers and Molecular Shapes 363
- 10.2 Bonding Theories 363
 - 10.2.1 Crystal Field Theory 364
- 10.3 Ligand Field Theory 365
 - 10.3.1 Molecular Orbitals for Octahedral Complexes 365
 - 10.3.2 Orbital Splitting and Electron Spin 372
 - 10.3.3 Ligand Field Stabilization Energy 374
 - 10.3.4 Square-Planar Complexes 377
 - 10.3.5 Tetrahedral Complexes 381
- 10.4 Angular Overlap 382
 - 10.4.1 Sigma-Donor Interactions 383
 - 10.4.2 Pi-Acceptor Interactions 385
 - 10.4.3 Pi-Donor Interactions 387
 - 10.4.4 The Spectrochemical Series 388
 - 10.4.5 Magnitudes of e_{σ} , e_{π} , and Δ 389
 - 10.4.6 A Magnetochemical Series 392

10.5 The Jahn–Teller Effect 393

10.6 Four- and Six-Coordinate Preferences 394

10.7 Other Shapes 397

General References 398 • *Problems* 399

Chapter 11

Coordination Chemistry III: Electronic Spectra 403

- 11.1 Absorption of Light 403
 - 11.1.1 Beer–Lambert Absorption Law 404
- 11.2 Quantum Numbers of Multielectron Atoms 405
 - 11.2.1 Spin–Orbit Coupling 411
- 11.3 Electronic Spectra of Coordination Compounds 412
 - 11.3.1 Selection Rules 414
 - 11.3.2 Correlation Diagrams 415
 - 11.3.3 Tanabe–Sugano Diagrams 417
 - 11.3.4 Jahn–Teller Distortions and Spectra 422
 - 11.3.5 Applications of Tanabe–Sugano Diagrams: Determining Δ_o from Spectra 425
 - 11.3.6 Tetrahedral Complexes 429
 - 11.3.7 Charge-Transfer Spectra 430
 - 11.3.8 Charge-Transfer and Energy Applications 431

General References 434 • Problems 434

Chapter 12

Coordination Chemistry IV: Reactions and Mechanisms 437

- 12.1 Background 437
- 12.2 Substitution Reactions 439
 - 12.2.1 Inert and Labile Compounds 439
 - 12.2.2 Mechanisms of Substitution 441
- 12.3 Kinetic Consequences of Reaction Pathways 441
 - 12.3.1 Dissociation (*D*) 442
 - 12.3.2 Interchange (*I*) 443
 - 12.3.3 Association (*A*) 443
 - 12.3.4 Preassociation Complexes 444
- 12.4 Experimental Evidence in Octahedral Substitution 445
 - 12.4.1 Dissociation 445
 - 12.4.2 Linear Free-Energy Relationships 447
 - 12.4.3 Associative Mechanisms 449
 - 12.4.4 The Conjugate Base Mechanism 450
 - 12.4.5 The Kinetic Chelate Effect 452
- 12.5 Stereochemistry of Reactions 452
 - 12.5.1 Substitution in *trans* Complexes 453
 - 12.5.2 Substitution in *cis* Complexes 455
 - 12.5.3 Isomerization of Chelate Rings 456
- 12.6 Substitution Reactions of Square-Planar Complexes 457
 - 12.6.1 Kinetics and Stereochemistry of Square-Planar Substitutions 457
 - 12.6.2 Evidence for Associative Reactions 458
- 12.7 The *trans* Effect 460
 - 12.7.1 Explanations of the *trans* Effect 461
- 12.8 Oxidation–Reduction Reactions 462
 - 12.8.1 Inner-Sphere and Outer-Sphere Reactions 463
 - 12.8.2 Conditions for High and Low Oxidation Numbers 467
- 12.9 Reactions of Coordinated Ligands 468
 - 12.9.1 Hydrolysis of Esters, Amides, and Peptides 468
 - 12.9.2 Template Reactions 469
 - 12.9.3 Electrophilic Substitution 470

General References 471 • Problems 472

Chapter 13

Organometallic Chemistry 475

- 13.1 Historical Background 476
- 13.2 Organic Ligands and Nomenclature 479

13.3 The 18-Electron Rule	480
13.3.1 Counting Electrons	480
13.3.2 Why 18 Electrons?	483
13.3.3 Square-Planar Complexes	485
13.4 Ligands in Organometallic Chemistry	486
13.4.1 Carbonyl (CO) Complexes	486
13.4.2 Ligands Similar to CO	493
13.4.3 Hydride and Dihydrogen Complexes	495
13.4.4 Ligands Having Extended Pi Systems	496
13.5 Bonding between Metal Atoms and Organic Pi Systems	500
13.5.1 Linear Pi Systems	500
13.5.2 Cyclic Pi Systems	502
13.5.3 Fullerene Complexes	509
13.6 Complexes Containing M—C, M=C, and M≡C Bonds	513
13.6.1 Alkyl and Related Complexes	513
13.6.2 Carbene Complexes	515
13.6.3 Carbyne (Alkylidyne) Complexes	517
13.6.4 Carbide and Cumulene Complexes	518
13.6.5 Carbon Wires: Polyyne and Polyene Bridges	519
13.7 Covalent Bond Classification Method	520
13.8 Spectral Analysis and Characterization of Organometallic Complexes	524
13.8.1 Infrared Spectra	524
13.8.2 NMR Spectra	527
13.8.3 Examples of Characterization	529
<i>General References</i>	534 • <i>Problems</i> 534

Chapter 14

Organometallic Reactions and Catalysis	541
14.1 Reactions Involving Gain or Loss of Ligands	541
14.1.1 Ligand Dissociation and Substitution	541
14.1.2 Oxidative Addition and C—H Bond Activation	545
14.1.3 Reductive Elimination and Pd-Catalyzed Cross-Coupling	547
14.1.4 Sigma Bond Metathesis	549
14.1.5 Application of Pincer Ligands	549
14.2 Reactions Involving Modification of Ligands	550
14.2.1 Insertion	550
14.2.2 Carbonyl Insertion (Alkyl Migration)	550
14.2.3 Examples of 1,2 Insertions	553
14.2.4 Hydride Elimination	554
14.2.5 Abstraction	555
14.3 Organometallic Catalysts	555
14.3.1 Catalytic Deuteration	556
14.3.2 Hydroformylation	556
14.3.3 Monsanto Acetic Acid Process	561
14.3.4 Wacker (Smidt) Process	562
14.3.5 Hydrogenation by Wilkinson's Catalyst	563
14.3.6 Olefin Metathesis	565
14.4 Heterogeneous Catalysts	570
14.4.1 Ziegler–Natta Polymerizations	570
14.4.2 Water Gas Reaction	571
<i>General References</i>	574 • <i>Problems</i> 574

Chapter 15

Parallels between Main Group and Organometallic Chemistry	579
15.1 Main Group Parallels with Binary Carbonyl Complexes	579
15.2 The Isolobal Analogy	581
15.2.1 Extensions of the Analogy	584
15.2.2 Examples of Applications of the Analogy	588

15.3 Metal–Metal Bonds	590
15.3.1 Multiple Metal–Metal Bonds	591
15.4 Cluster Compounds	596
15.4.1 Boranes	596
15.4.2 Heteroboranes	602
15.4.3 Metallaboranes and Metallacarboranes	604
15.4.4 Carbonyl Clusters	607
15.4.5 Carbon-Centered Clusters	611
15.4.6 Additional Comments on Clusters	612

General References 614 • *Problems* 614

Appendix A Answers to Exercises 619

Appendix B Useful Data

App. B can be found online at www.pearsonhighered.com/advchemistry

Appendix B.1 Ionic Radii

Appendix B.2 Ionization Energy

Appendix B.3 Electron Affinity

Appendix B.4 Electronegativity

Appendix B.5 Absolute Hardness Parameters

Appendix B.6 C_A , E_A , C_B , and E_B Values

Appendix B.7 Latimer Diagrams for Selected Elements

Appendix B.8 Angular Functions for Hydrogen Atom f Orbitals

Appendix B.9 Orbital Potential Energies

Appendix C Character Tables 658

Index 668



Preface

The rapid development of inorganic chemistry makes ever more challenging the task of providing a textbook that is contemporary and meets the needs of those who use it. We appreciate the constructive suggestions provided by students, faculty, and reviewers, and have adopted much of this advice, keeping in mind the constraints imposed by space and the scope of the book. The main emphasis in preparing this edition has been to bring it up to date while providing clarity and a variety of helpful features.

New to the Fifth Edition:

- New and expanded discussions have been incorporated in many chapters to reflect topics of contemporary interest: for example, frustrated Lewis pairs (Chapter 6), IUPAC guidelines defining hydrogen bonds (Chapter 6), multiple bonding between Group 13 elements (Chapter 8), graphyne (Chapter 8), developments in noble gas chemistry (Chapter 8), metal–organic frameworks (Chapter 9), pincer ligands (Chapter 9), the magnetochemical series (Chapter 10), photosensitizers (Chapter 11), polyynes and polyene carbon “wires” (Chapter 13), percent buried volume of ligands (Chapter 14), and introductions to C–H bond activation, Pd-catalyzed cross-coupling, and sigma-bond metathesis (Chapter 14).
- To better represent the shapes of molecular orbitals, we are providing new images, generated by molecular modeling software, for most of the orbitals presented in Chapter 5.
- In a similar vein, to more accurately depict the shapes of many molecules, we have generated new images using CIF files from available crystal structure determinations. We hope that readers will find these images a significant improvement over the line drawings and ORTEP images that they replace.
- The discussion of electronegativity in connection with the VSEPR model in Chapter 3 has been expanded, and group electronegativity has been added.
- In response to users’ requests, the projection operator approach has been added in the context of molecular orbitals of nonlinear molecules in Chapter 5. Chapter 8 includes more elaboration on Frost diagrams, and additional magnetic susceptibility content has been incorporated into Chapter 10.
- Chapter 6 has been reorganized to highlight contemporary aspects of acid–base chemistry and to include a broader range of measures of relative strengths of acids and bases.
- In Chapter 9 numerous new images have been added to provide more contemporary examples of the geometries of coordination complexes and coordination frameworks.
- The Covalent Bond Classification Method and MLX plots are now introduced in Chapter 13.
- Approximately 15% of end-of-chapter problems are new, with most based on the recent inorganic literature. To further encourage in-depth engagement with the literature, more problems involving extracting and interpreting information from the literature have been included. The total number of problems is more than 580.

- The values of physical constants inside the back cover have been revised to use the most recent values cited on the NIST Web site.
- This edition expands the use of color to better highlight the art and chemistry within the text and to improve readability of tables.

The need to add new material to keep up with the pace of developments in inorganic chemistry while maintaining a reasonable length is challenging, and difficult content decisions must be made. To permit space for increased narrative content while not significantly expanding the length of the book, Appendix B, containing tables of numerical data, has been placed online for free access.

We hope that the text will serve readers well. We will appreciate feedback and advice as we look ahead to edition 6.

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For the Student

SOLUTIONS MANUAL (ISBN: 0321814134) by Gary L. Miessler, Paul J. Fischer, and Donald A. Tarr. This manual includes fully worked-out solutions to all end-of-chapter problems in the text.

Dedication and Acknowledgments

We wish to dedicate this textbook to our doctoral research advisors Louis H. Pignolet (Miessler) and John E. Ellis (Fischer) on the occasion of their seventieth birthdays. These chemists have inspired us throughout their careers by their exceptional creativity for chemical synthesis and dedication to the discipline of scholarship. We are grateful to have been trained by these stellar witnesses to the vocation of inorganic chemistry.

We thank Kaitlin Hellie for generating molecular orbital images (Chapter 5), Susan Green for simulating photoelectron spectra (Chapter 5), Zoey Rose Herm for generating images of metal–organic frameworks (Chapter 9), and Laura Avena for assistance with images generated from CIF files. We are also grateful to Sophia Hayes for useful advice on projection operators and Robert Rossi and Gerard Parkin for helpful discussions. We would also like to thank Andrew Mobley (Grinnell College), Dave Finster (Wittenberg University) and Adam Johnson (Harvey Mudd College) for their accuracy review of our text. We appreciate all that Jeanne Zalesky and Coleen Morrison, our editors at Pearson, and Jacki Russell at GEX Publishing Services have contributed.

Finally, we greatly value the helpful suggestions of the reviewers and other faculty listed below and of the many students at St. Olaf College and Macalester College who have pointed out needed improvements. While not all suggestions could be included because of constraints on the scope and length of the text, we are grateful for the many individuals who have offered constructive feedback. All of these ideas improve our teaching of inorganic chemistry and will be considered anew for the next edition.

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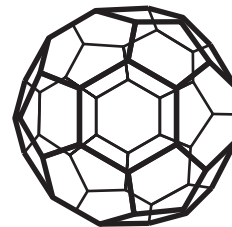
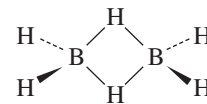
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Introduction to Inorganic Chemistry



1.1 What Is Inorganic Chemistry?

If organic chemistry is defined as the chemistry of hydrocarbon compounds and their derivatives, inorganic chemistry can be described broadly as the chemistry of “everything else.” This includes all the remaining elements in the periodic table, as well as carbon, which plays a major and growing role in inorganic chemistry. The large field of organometallic chemistry bridges both areas by considering compounds containing metal–carbon bonds; it also includes catalysis of many organic reactions. Bioinorganic chemistry bridges biochemistry and inorganic chemistry and has an important focus on medical applications. Environmental chemistry includes the study of both inorganic and organic compounds. In short, the inorganic realm is vast, providing essentially limitless areas for investigation and potential practical applications.

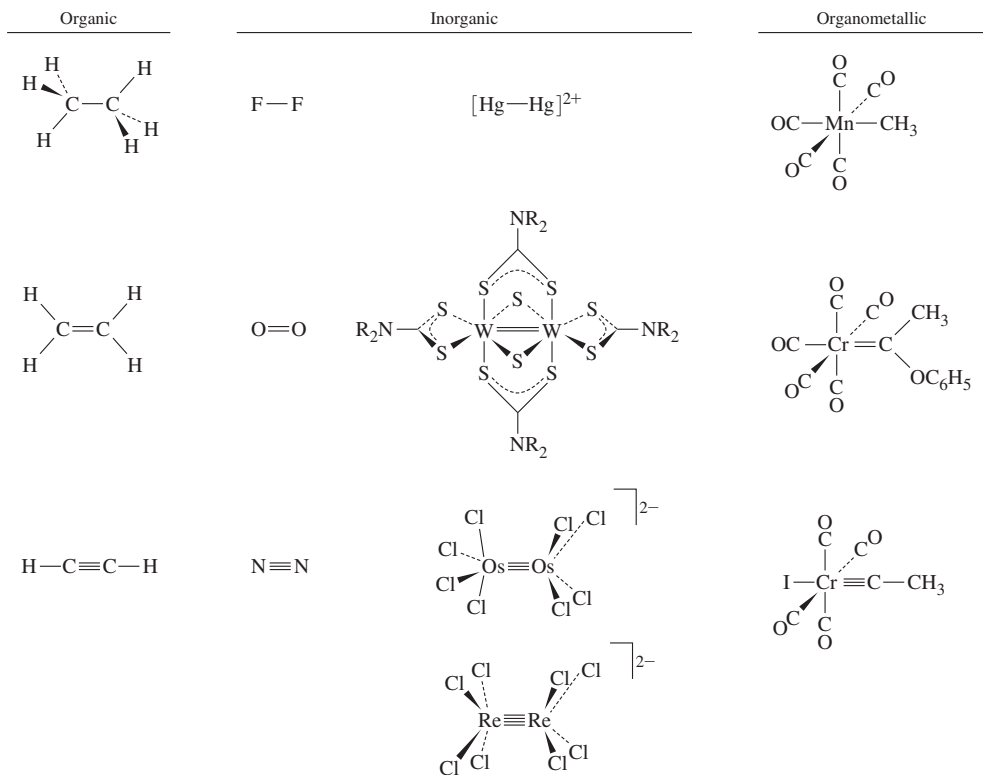
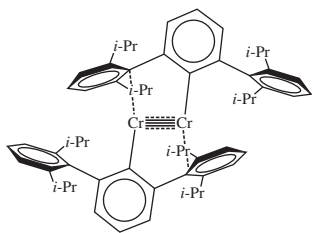
1.2 Contrasts with Organic Chemistry

Some comparisons between organic and inorganic compounds are in order. In both areas, single, double, and triple covalent bonds are found (**Figure 1.1**); for inorganic compounds, these include direct metal–metal bonds and metal–carbon bonds. Although the maximum number of bonds between two carbon atoms is three, there are many compounds that contain quadruple bonds between metal atoms. In addition to the sigma and pi bonds common in organic chemistry, quadruply bonded metal atoms contain a delta (δ) bond (**Figure 1.2**); a combination of one sigma bond, two pi bonds, and one delta bond makes up the quadruple bond. The delta bond is possible in these cases because the metal atoms have *d* orbitals to use in bonding, whereas carbon has only *s* and *p* orbitals energetically accessible for bonding.

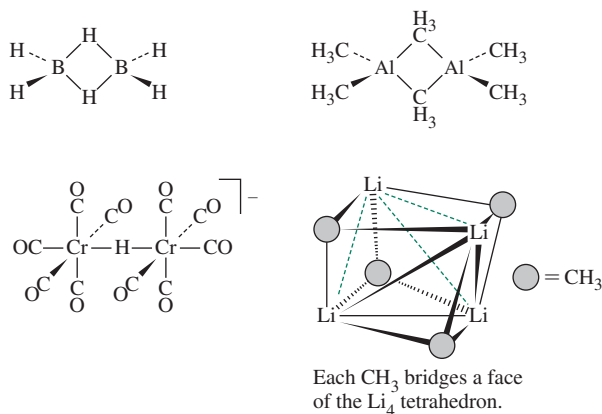
Compounds with “fivefold” bonds between transition metals have been reported (**Figure 1.3**), accompanied by debate as to whether these bonds merit the designation “quintuple.”

In organic compounds, hydrogen is nearly always bonded to a single carbon. In inorganic compounds, hydrogen is frequently encountered as a bridging atom between two or more other atoms. Bridging hydrogen atoms can also occur in metal cluster compounds, in which hydrogen atoms form bridges across edges or faces of polyhedra of metal atoms. Alkyl groups may also act as bridges in inorganic compounds, a function rarely encountered in organic chemistry except in reaction intermediates. Examples of terminal and bridging hydrogen atoms and alkyl groups in inorganic compounds are in **Figure 1.4**.

Some of the most striking differences between the chemistry of carbon and that of many other elements are in coordination number and geometry. Although carbon is usually limited to a maximum coordination number of four (a maximum of four atoms bonded

FIGURE 1.1 Single and Multiple Bonds in Organic and Inorganic Molecules.**FIGURE 1.2** Examples of Bonding Interactions.**FIGURE 1.3** Example of Fivefold Bonding.

to carbon, as in CH_4), numerous inorganic compounds have central atoms with coordination numbers of five, six, seven, and higher; the most common coordination geometry for transition metals is an octahedral arrangement around a central atom, as shown for $[TiF_6]^{3-}$ (Figure 1.5). Furthermore, inorganic compounds present coordination geometries different from those found for carbon. For example, although 4-coordinate carbon is nearly always tetrahedral, both tetrahedral and square-planar shapes occur for 4-coordinate compounds of both metals and nonmetals. When metals are in the center, with anions or neutral molecules (*ligands*) bonded to them (frequently through N, O, or S), these are called *coordination complexes*; when carbon is the element directly bonded to metal atoms or ions, they are also classified as *organometallic* complexes.

**FIGURE 1.4** Examples of Inorganic Compounds Containing Terminal and Bridging Hydrogens and Alkyl Groups.

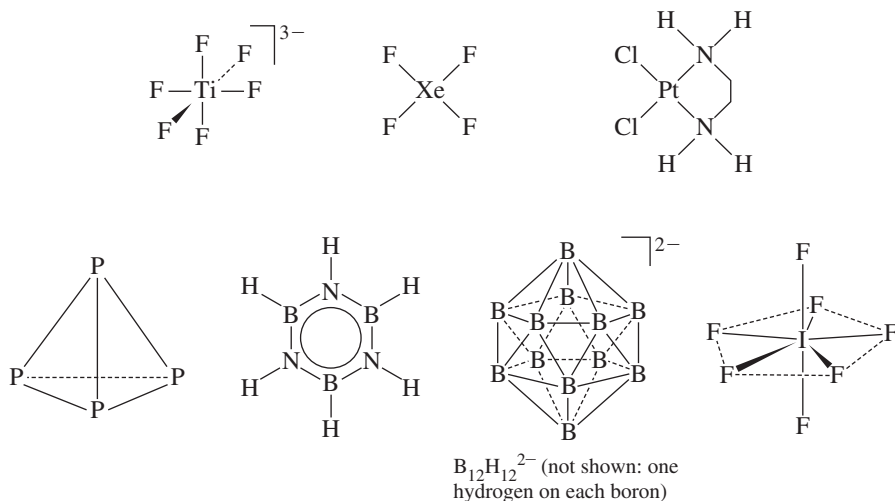


FIGURE 1.5 Examples of Geometries of Inorganic Compounds.

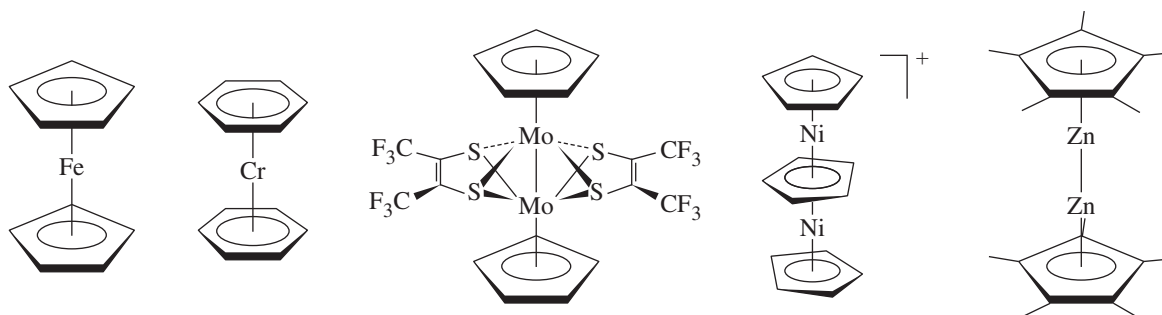


FIGURE 1.6 Inorganic Compounds Containing Pi-Bonded Aromatic Rings.

The tetrahedral geometry usually found in 4-coordinate compounds of carbon also occurs in a different form in some inorganic molecules. Methane contains four hydrogens in a regular tetrahedron around carbon. Elemental phosphorus is tetratomic (P_4) and tetrahedral, but with no central atom. Other elements can also form molecules in which outer atoms surround a central cavity; an example is boron, which forms numerous structures containing icosahedral B_{12} units. Examples of some of the geometries found for inorganic compounds are in Figure 1.5.

Aromatic rings are common in organic chemistry, and aryl groups can also form sigma bonds to metals. However, aromatic rings can also bond to metals in a dramatically different fashion using their pi orbitals, as shown in Figure 1.6 and in this book's cover illustration. The result is a metal atom bonded above the center of the ring, almost as if suspended in space. In many cases, metal atoms are sandwiched between two aromatic rings. Multiple-decker sandwiches of metals and aromatic rings are also known.

Carbon plays an unusual role in a number of metal *cluster compounds* in which a carbon atom is at the center of a polyhedron of metal atoms. Examples of carbon-centered clusters with five, six, or more surrounding metals are known (Figure 1.7). The striking role that carbon plays in these clusters has provided a challenge to theoretical inorganic chemists.

In addition, since the mid-1980s the chemistry of elemental carbon has flourished. This phenomenon began with the discovery of fullerenes, most notably the cluster C_{60} , dubbed “buckminsterfullerene” after the developer of the geodesic dome. Many other fullerenes (buckyballs) are now known and serve as cores of a variety of derivatives. In

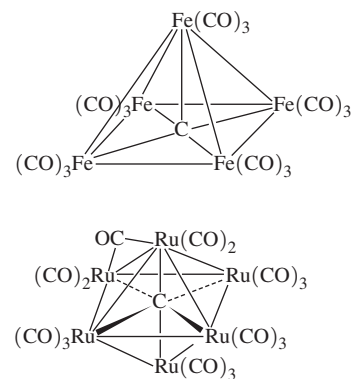
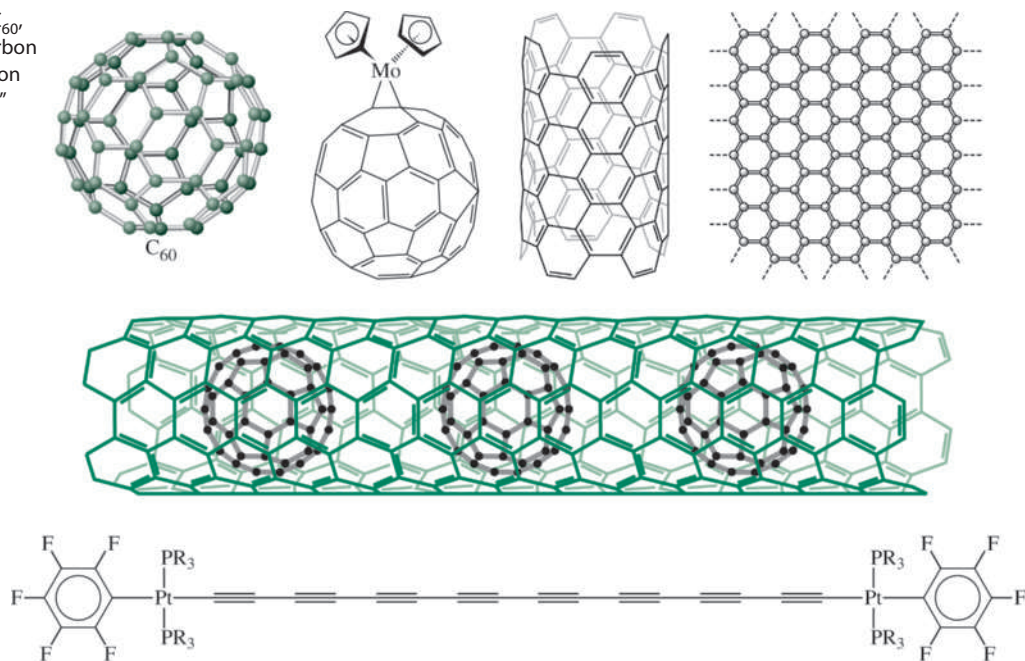


FIGURE 1.7 Carbon-Centered Metal Clusters.

FIGURE 1.8 The Fullerene C_{60} , a Fullerene Compound, a Carbon Nanotube, Graphene, a Carbon Peapod, and a Polyynyl “Wire” Connecting Platinum Atoms.



addition, numerous other forms of carbon (for example, carbon nanotubes, nanoribbons, graphene, and carbon wires) have attracted much interest and show potential for applications in fields as diverse as nanoelectronics, body armor, and drug delivery. **Figure 1.8** provides examples of these newer forms of carbon.

The era of sharp dividing lines between subfields in chemistry has long been obsolete. Many of the subjects in this book, such as acid–base chemistry and organometallic reactions, are of vital interest to organic chemists. Other topics such as oxidation–reduction reactions, spectra, and solubility relations interest analytical chemists. Subjects related to structure determination, spectra, conductivity, and theories of bonding appeal to physical chemists. Finally, the use of organometallic catalysts provides a connection to petroleum and polymer chemistry, and coordination compounds such as hemoglobin and metal-containing enzymes provide a similar tie to biochemistry. Many inorganic chemists work with professionals in other fields to apply chemical discoveries to addressing modern challenges in medicine, energy, the environment, materials science, and other fields. In brief, modern inorganic chemistry is not a fragmented field of study, but has numerous interconnections with other fields of science, medicine, technology, and other disciplines.

The remainder of this chapter is devoted to a short history of the origins of inorganic chemistry and perspective on more recent developments, intended to provide a sense of connection to the past and to place some aspects of inorganic chemistry within the context of larger historical events. In later chapters, brief historical context is provided with the same intention.

1.3 The History of Inorganic Chemistry

Even before alchemy became a subject of study, many chemical reactions were used and their products applied to daily life. The first metals used were probably gold and copper, which can be found in the metallic state in nature. Copper can also be readily formed by the reduction of malachite—basic copper carbonate, $Cu_2(CO_3)(OH)_2$ —in charcoal fires. Silver, tin, antimony, and lead were also known as early as 3000 BCE. Iron appeared in

classical Greece and in other areas around the Mediterranean Sea by 1500 BCE. At about the same time, colored glasses and ceramic glazes were introduced, largely composed of silicon dioxide (SiO_2 , the major component of sand) and other metallic oxides, which had been melted and allowed to cool to amorphous solids.

Alchemists were active in China, Egypt, and other centers of civilization early in the first centuries CE. Although much effort went into attempts to “transmute” base metals into gold, alchemists also described many other chemical reactions and operations. Distillation, sublimation, crystallization, and other techniques were developed and used in their studies. Because of the political and social changes of the time, alchemy shifted into the Arab world and later—about 1000 to 1500 CE—reappeared in Europe. Gunpowder was used in Chinese fireworks as early as 1150, and alchemy was also widespread in China and India at that time. Alchemists appeared in art, literature, and science until at least 1600, by which time chemistry was beginning to take shape as a science. Roger Bacon (1214–1294), recognized as one of the first great experimental scientists, also wrote extensively about alchemy.

By the seventeenth century, the common strong acids—nitric, sulfuric, and hydrochloric—were known, and systematic descriptions of common salts and their reactions were being accumulated. As experimental techniques improved, the quantitative study of chemical reactions and the properties of gases became more common, atomic and molecular weights were determined more accurately, and the groundwork was laid for what later became the periodic table of the elements. By 1869, the concepts of atoms and molecules were well established, and it was possible for Mendeleev and Meyer to propose different forms of the periodic table. **Figure 1.9** illustrates Mendeleev’s original periodic table.*

The chemical industry, which had been in existence since very early times in the form of factories for purifying salts and for smelting and refining metals, expanded as methods for preparing relatively pure materials became common. In 1896, Becquerel discovered radioactivity, and another area of study was opened. Studies of subatomic particles, spectra, and electricity led to the atomic theory of Bohr in 1913, which was soon modified by the quantum mechanics of Schrödinger and Heisenberg in 1926 and 1927.

Inorganic chemistry as a field of study was extremely important during the early years of the exploration and development of mineral resources. Qualitative analysis methods were

			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	Ta = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 53	Rh = 104.4	Pt = 197.4
			Fe = 56	Ru = 104.2	Ir = 198
			Ni = Co = 59	Pd = 106.6	Os = 199
			Cu = 63.4	Ag = 108	Hg = 200
H = 1	Be = 9.4	Mg = 24	Zn = 65.2	Cd = 112	
	B = 11	Al = 27.4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
	O = 16	S = 32	Se = 79.4	Te = 128?	
	F = 19	Cl = 35.5	Br = 80	J = 127	
Li = 7	Na = 23	K = 39	Rb = 85.4	Cs = 133	Tl = 204
		Ca = 40	Sr = 87.6	Ba = 137	Pb = 207
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75.6	Th = 118 ?		

FIGURE 1.9 Mendeleev’s 1869 Periodic Table. Two years later, Mendeleev revised his table into a form similar to a modern short-form periodic table, with eight groups across.

*The original table was published in *Zeitschrift für Chemie*, **1869**, 12, 405. It can be found in English translation, together with a page from the German article, at web.lemoyne.edu/~giunta/mendeleev.html. See M. Laing, *J. Chem. Educ.*, **2008**, 85, 63 for illustrations of Mendeleev’s various versions of the periodic table, including his handwritten draft of the 1869 table.

developed to help identify minerals and, combined with quantitative methods, to assess their purity and value. As the Industrial Revolution progressed, so did the chemical industry. By the early twentieth century, plants for the high volume production of ammonia, nitric acid, sulfuric acid, sodium hydroxide, and many other inorganic chemicals were common.

Early in the twentieth century, Werner and Jørgensen made considerable progress on understanding the coordination chemistry of transition metals and also discovered a number of organometallic compounds. Nevertheless, the popularity of inorganic chemistry as a field of study gradually declined during most of the first half of the century. The need for inorganic chemists to work on military projects during World War II rejuvenated interest in the field. As work was done on many projects (not least of which was the Manhattan Project, in which scientists developed the fission bomb), new areas of research appeared, and new theories were proposed that prompted further experimental work. A great expansion of inorganic chemistry began in the 1940s, sparked by the enthusiasm and ideas generated during World War II.

In the 1950s, an earlier method used to describe the spectra of metal ions surrounded by negatively charged ions in crystals (**crystal field theory**)¹ was extended by the use of molecular orbital theory² to develop **ligand field theory** for use in coordination compounds, in which metal ions are surrounded by ions or molecules that donate electron pairs. This theory gave a more complete picture of the bonding in these compounds. The field developed rapidly as a result of this theoretical framework, availability of new instruments, and the generally reawakened interest in inorganic chemistry.

In 1955, Ziegler³ and Natta⁴ discovered organometallic compounds that could catalyze the polymerization of ethylene at lower temperatures and pressures than the common industrial method at that time. In addition, the polyethylene formed was more likely to be made up of linear, rather than branched, molecules and, as a consequence, was stronger and more durable. Other catalysts were soon developed, and their study contributed to the rapid expansion of organometallic chemistry, still a rapidly growing area.

The study of biological materials containing metal atoms has also progressed rapidly. The development of new experimental methods allowed more thorough study of these compounds, and the related theoretical work provided connections to other areas of study. Attempts to make *model* compounds that have chemical and biological activity similar to the natural compounds have also led to many new synthetic techniques. Two of the many biological molecules that contain metals are in **Figure 1.10**. Although these molecules have very different roles, they share similar ring systems.

One current area that bridges organometallic chemistry and bioinorganic chemistry is the conversion of nitrogen to ammonia:



This reaction is one of the most important industrial processes, with over 100 million tons of ammonia produced annually worldwide, primarily for fertilizer. However, in spite of metal oxide catalysts introduced in the Haber–Bosch process in 1913, and improved since then, it is also a reaction that requires temperatures between 350 and 550 °C and from 150–350 atm pressure and that still results in a yield of only 15 percent ammonia. Bacteria, however, manage to fix nitrogen (convert it to ammonia and then to nitrite and nitrate) at 0.8 atm at room temperature in nodules on the roots of legumes. The nitrogenase enzyme that catalyzes this reaction is a complex iron–molybdenum–sulfur protein. The structure of its active sites has been determined by X-ray crystallography.⁵ A vigorous area of modern inorganic research is to design reactions that could be carried out on an industrial scale that model the reaction of nitrogenase to generate ammonia under mild conditions. It is estimated that as much as 1 percent of the world's total energy consumption is currently used for the Haber–Bosch process.

Inorganic chemistry also has medical applications. Notable among these is the development of platinum-containing antitumor agents, the first of which was the *cis* isomer of Pt(NH₃)₂Cl₂,

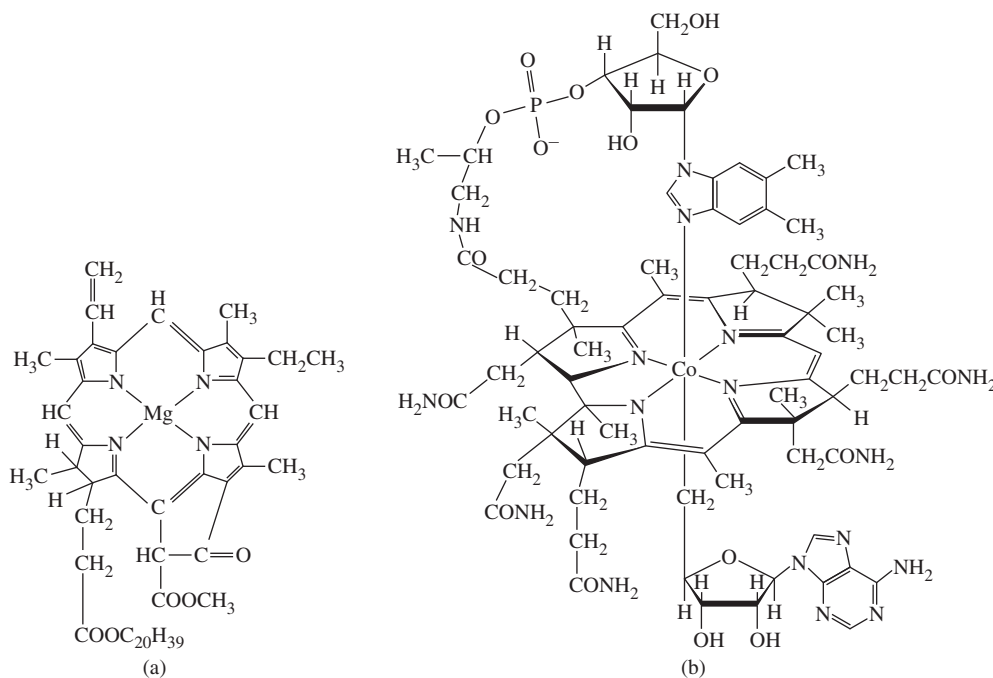


FIGURE 1.10 Biological Molecules Containing Metal Ions. (a) Chlorophyll a, the active agent in photosynthesis. (b) Vitamin B₁₂ coenzyme, a naturally occurring organometallic compound.

cisplatin. First approved for clinical use approximately 30 years ago, cisplatin has served as the prototype for a variety of anticancer agents; for example, satraplatin, the first orally available platinum anticancer drug to reach clinical trials.* These two compounds are in **Figure 1.11**.

1.4 Perspective

The premier issue of the journal *Inorganic Chemistry*** was published in February 1962. Much of the focus of that issue was on classic coordination chemistry, with more than half its research papers on synthesis of coordination complexes and their structures and properties. A few papers were on compounds of nonmetals and on organometallic chemistry, then a relatively new field; several were on thermodynamics or spectroscopy. All of these topics have developed considerably in the subsequent half-century, but much of the evolution of inorganic chemistry has been into realms unforeseen in 1962.

The 1962 publication of the first edition of F. A. Cotton and G. Wilkinson's landmark text *Advanced Inorganic Chemistry*⁶ provides a convenient reference point for the status of inorganic chemistry at that time. For example, this text cited only the two long-known forms of carbon, diamond and graphite, although it did mention "amorphous forms" attributed to microcrystalline graphite. It would not be until more than two decades later that carbon chemistry would explode with the seminal discovery of C₆₀ in 1985 by Kroto, Curl, Smalley, and colleagues,⁷ followed by other fullerenes, nanotubes, graphene, and other forms of carbon (Figure 1.8) with the potential to have major impacts on electronics, materials science, medicine, and other realms of science and technology.

As another example, at the beginning of 1962 the elements helium through radon were commonly dubbed "inert" gases, believed to "form no chemically bound compounds" because of the stability of their electron configurations. Later that same year, Bartlett

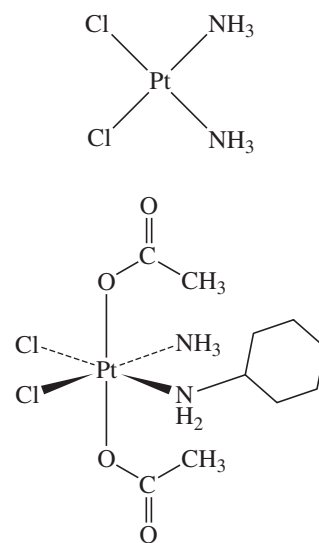


FIGURE 1.11 Cisplatin and Satraplatin.

*For reviews of modes of interaction of cisplatin and related drugs, see P. C. A. Bruijninx, P. J. Sadler, *Curr. Opin. Chem. Bio.*, **2008**, *12*, 197 and F. Arnesano, G. Natile, *Coord. Chem. Rev.*, **2009**, *253*, 2070.

**The authors of this issue of *Inorganic Chemistry* were a distinguished group, including five recipients of the Priestley Medal, the highest honor conferred by the American Chemical Society, and 1983 Nobel Laureate Henry Taube.

reported the first chemical reactions of xenon with PtF_6 , launching the synthetic chemistry of the now-renamed “noble” gas elements, especially xenon and krypton;⁸ numerous compounds of these elements have been prepared in succeeding decades.

Numerous square planar platinum complexes were known by 1962; the chemistry of platinum compounds had been underway for more than a century. However, it was not known until Rosenberg’s work in the latter part of the 1960s that one of these, $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ (cisplatin, Figure 1.11), had anticancer activity.⁹ Antitumor agents containing platinum and other transition metals have subsequently become major tools in treatment regimens for many types of cancer.¹⁰

That first issue of *Inorganic Chemistry* contained only 188 pages, and the journal was published quarterly, exclusively in hardcopy. Researchers from only four countries were represented, more than 90 percent from the United States, the others from Europe. *Inorganic Chemistry* now averages approximately 550 pages per issue, is published 24 times annually, and publishes (electronically) research conducted broadly around the globe. The growth and diversity of research published in *Inorganic Chemistry* has been paralleled in a wide variety of other journals that publish articles on inorganic and related fields.

In the preface to the first edition of *Advanced Inorganic Chemistry*, Cotton and Wilkinson stated, “in recent years, inorganic chemistry has experienced an impressive renaissance.” This renaissance shows no sign of diminishing.

With this brief survey of the marvelously complex field of inorganic chemistry, we now turn to the details in the remainder of this book. The topics included provide a broad introduction to the field. However, even a cursory examination of a chemical library or one of the many inorganic journals shows some important aspects of inorganic chemistry that must be omitted in a textbook of moderate length. The references cited in this text suggest resources for further study, including historical sources, texts, and reference works that provide useful additional material.

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General References

For those who are interested in the historical development of inorganic chemistry focused on metal coordination compounds during the period 1798–1935, copies of key research papers, including translations, are provided in the three-volume set *Classics in Coordination Chemistry*, G. B. Kauffman, ed., Dover Publications, N.Y. 1968, 1976, 1978. Among the many general reference works available, three of the most useful and complete are N. N. Greenwood and A. Earnshaw’s *Chemistry of*

the Elements, 2nd ed., Butterworth-Heinemann, Oxford, 1997; F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochman’s *Advanced Inorganic Chemistry*, 6th ed., John Wiley & Sons, New York, 1999; and A. F. Wells’s *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, New York, 1984. An interesting study of inorganic reactions from a different perspective can be found in G. Wulfsberg’s *Principles of Descriptive Inorganic Chemistry*, Brooks/Cole, Belmont, CA, 1987.

Atomic Structure



Understanding the structure of the atom has been a fundamental challenge for centuries. It is possible to gain a practical understanding of atomic and molecular structure using only a moderate amount of mathematics rather than the mathematical sophistication of quantum mechanics. This chapter introduces the fundamentals needed to explain atomic structure in qualitative and semiquantitative terms.

2.1 Historical Development of Atomic Theory

Although the Greek philosophers Democritus (460–370 BCE) and Epicurus (341–270 BCE) presented views of nature that included atoms, many centuries passed before experimental studies could establish the quantitative relationships needed for a coherent atomic theory. In 1808, John Dalton published *A New System of Chemical Philosophy*,¹ in which he proposed that

... the ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, etc. In other words, every particle of water is like every other particle of water; every particle of hydrogen is like every other particle of hydrogen, etc.²

and that atoms combine in simple numerical ratios to form compounds. The terminology he used has since been modified, but he clearly presented the concepts of atoms and molecules, and made quantitative observations of the masses and volumes of substances as they combined to form new substances. For example, in describing the reaction between the gases hydrogen and oxygen to form water Dalton said that

When two measures of hydrogen and one of oxygen gas are mixed, and fired by the electric spark, the whole is converted into steam, and if the pressure be great, this steam becomes water. It is most probable then that there is the same number of particles in two measures of hydrogen as in one of oxygen.³

Because Dalton was not aware of the diatomic nature of the molecules H_2 and O_2 , which he assumed to be monatomic H and O, he did not find the correct formula of water, and therefore his surmise about the relative numbers of particles in “measures” of the gases is inconsistent with the modern concept of the mole and the chemical equation $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$.

Only a few years later, Avogadro used data from Gay-Lussac to argue that equal volumes of gas at equal temperatures and pressures contain the same number of molecules, but uncertainties about the nature of sulfur, phosphorus, arsenic, and mercury vapors delayed acceptance of this idea. Widespread confusion about atomic weights and molecular formulas contributed to the delay; in 1861, Kekulé gave 19 different possible formulas for acetic acid!⁴ In the 1850s, Cannizzaro revived the argument of Avogadro and argued that