

Contents

Preface *xi*

Part I Introduction *1*

1	Historical Background	<i>3</i>
	<i>Amol Singh, Himadri Priya Gogoi, and Pranjit Barman</i>	
1.1	Introduction	<i>3</i>
1.2	Theories of Coordinate Bond	<i>4</i>
1.2.1	Valence Bond Theory	<i>4</i>
1.2.2	Crystal Field Theory	<i>4</i>
1.2.3	Molecular Orbital Theory	<i>5</i>
1.2.4	Ligand Field Theory	<i>6</i>
	References	<i>7</i>
2	Classification	<i>9</i>
	<i>Amol Singh, Himadri Priya Gogoi, and Pranjit Barman</i>	
2.1	Ligands	<i>9</i>
2.2	Schiff Base	<i>9</i>
2.3	Types of Schiff Base	<i>12</i>
2.3.1	Salen-type Ligands	<i>12</i>
2.3.2	Salophen-type Ligands	<i>12</i>
2.3.3	Hydrazone-type Ligands	<i>12</i>
2.3.4	Thiosemicarbazone/Carbazone-type Ligands	<i>13</i>
2.3.5	Heterocyclic Schiff Bases	<i>14</i>
2.4	Different Bonding Modes of Schiff Bases	<i>14</i>
2.4.1	Monodentate	<i>14</i>
2.4.2	Bidentate	<i>15</i>
2.4.3	Tridentate	<i>15</i>
2.4.4	Tetradentate	<i>16</i>
2.4.5	Pentadentate	<i>17</i>
2.4.6	Hexadentate	<i>17</i>
	References	<i>17</i>

3	Different Routes of Synthesis	23
	<i>Anmol Singh, Himadri Priya Gogoi, and Pranjit Barman</i>	
3.1	Formation of Schiff Bases	23
3.1.1	Direct Ligand Synthesis	24
3.1.2	Template Synthesis	25
3.1.3	Rearrangement of Heterocycles (Oxazoles, Thiazoles, etc.)	26
	References	26
4	Schiff Base Metal Complexes	29
	<i>Anmol Singh, Himadri Priya Gogoi, and Pranjit Barman</i>	
	References	34
5	Effect of Different Parameters on Schiff Base and their Metal Complex	37
	<i>Anmol Singh, Himadri Priya Gogoi, and Pranjit Barman</i>	
5.1	Ionic Charge	37
5.2	Ionic Size	37
5.3	Nature of Central Metal Ions	37
5.4	Nature of the Ligand	37
5.4.1	Basic Character of the Ligand	38
5.4.2	Size and Charge of the Ligand	38
5.4.3	Concentration of Ligand	38
5.4.4	Substitution Effect	38
5.4.5	Chelating Effect	39
5.4.6	Nature of Solvent	39
5.4.7	Crystal Field Effect	39
5.4.8	Thermodynamic and Kinetic Effect	39
	References	40
6	Thioether and Chiral Schiff Base	41
	<i>Anmol Singh, Himadri Priya Gogoi, and Pranjit Barman</i>	
6.1	Thioether Schiff Base	41
6.2	Chiral Schiff Base	44
	References	45
	Part II Synthesis	53
7	General Routes of Synthesis	55
	<i>Himadri Priya Gogoi, Anmol Singh, and Pranjit Barman</i>	
7.1	Introduction	55
7.2	Mechanism of the Synthesis of Schiff Base Ligand	56
7.3	Problems Found in Conventional Method – Hydrolysis of C=N Bond	59
	References	59

8	Different Route of Synthesis of Schiff Base-Metal Complexes	61
	<i>Himadri Priya Gogoi, Anmol Singh, and Pranjit Barman</i>	
8.1	Introduction	61
8.2	Different Chemical Routes	61
8.2.1	Preparation of Schiff's Bases via Aerobic Oxidative Synthesis	61
8.2.2	Synthesis of Schiff Bases via Addition of Organometallic Reagents to Cyanides	61
8.2.3	Reaction of Phenol with Nitriles to Form SB	62
8.2.4	Reaction of Metal Amides to Ketone to Form SB	63
8.2.5	Reaction of Nitroso Compounds with Active Hydrogen Compounds	63
8.2.6	Dehydrogenation of Amines	64
8.2.7	Oxidation of Metal Amines to Form SB	64
8.2.8	Reduction of Carbon–Nitrogen Compounds	65
8.2.9	Synthesis of SB from Ketals	65
8.2.10	SB Synthesis by Using Hydrazoic Acid	66
8.2.11	SB Synthesis by Using Sodium Hypochlorite	66
8.2.12	Preparation of <i>N</i> -metallo Imines	66
8.2.13	Preparation of <i>N</i> -metallo Imines (Metal = B, Al, Si, Sn)	67
8.2.13.1	Preparation of <i>N</i> -boryl and <i>N</i> -aluminum Imines	67
8.2.13.2	Preparation of <i>N</i> -silylimines via	67
8.2.13.3	Preparation of <i>N</i> -tin Imines	68
8.3	Different Methods	68
8.3.1	Classical or Conventional Method	69
8.3.2	Microwave Irradiation Method	70
8.3.3	Water as Solvent Method	71
8.3.4	Grindstone Technique	71
8.3.5	Ultrasonic Method	72
8.3.6	Green Method Using Green Catalyst	73
	References	76
9	Synthesis and Mechanism of Schiff Base-Metal Complexes	79
	<i>Himadri Priya Gogoi, Anmol Singh, and Pranjit Barman</i>	
9.1	Introduction	79
9.2	Synthesis of Schiff Bases Metal Complexes	79
9.2.1	Synthesis of Ligand Followed by Complexation	79
9.2.1.1	One-Step Process or Template Synthesis	80
9.3	Synthesis of Some of the Schiff Base Metal Complexes	83
	References	86
10	Synthesis and Mechanism of Chiral and Achiral Schiff Base and Their Metal Complexes	89
	<i>Himadri Priya Gogoi, Anmol Singh, and Pranjit Barman</i>	
10.1	Introduction	89
10.2	Synthesis of Chiral and Achiral SB Ligand	90

10.3	Synthesis of Chiral SB Metal Complexes	93
10.4	Chiral Schiff Bases of Titanium, Zirconium, and Vanadium	95
10.5	Chiral Schiff Bases of Main Group Metals	96
10.5.1	Manganese and Chromium Schiff Bases	97
10.5.2	Iron and Ruthenium Schiff Base Complexes	98
10.5.3	Cobalt, Nickel, Copper, and Zinc Schiff Base Complexes	98
10.5.4	Lanthanide Metal Schiff Bases	99
10.5.5	Silicon and Tin Metal Schiff Bases	99
	References	102
11	Synthesis and Mechanism of Thioether: Schiff Base and Their Metal Complexes	105
	<i>Himadri Priya Gogoi, Anmol Singh, and Pranjit Barman</i>	
11.1	Introduction	105
11.2	Chemical Synthesis Procedures	106
11.2.1	Procedure for the Synthesis of Thioether-Containing Schiff Base	106
	References	111
12	Computational Chemistry	113
	<i>Anmol Singh, Himadri Priya Gogoi, and Pranjit Barman</i>	
12.1	Introduction	113
12.2	Application of DFT in the Field of Schiff Base and Their Metal Complexes	115
	References	118
	Part III Application	119
13	General Applications of Schiff Bases and Their Metal Complexes	121
	<i>Anmol Singh, Himadri Priya Gogoi, and Pranjit Barman</i>	
13.1	Catalyst	121
13.2	Biological and Medicinal Importance	122
13.2.1	Antibacterial Activity	122
13.2.2	Anticancer and Anti-inflammatory Agent	122
13.2.3	Antifungal Activity	123
13.2.4	As a Drug in a Number of Diseases	123
13.3	Coatings	123
13.4	Analytical Chemistry	123
13.5	Dyes	124
13.6	Semi-conducting Materials	124
13.7	Solar System	124
13.8	Photocatalyst	125
13.9	Polymer Chemistry	125
13.10	Agrochemical Industry	125
	References	125

- 14 Application in Pharmacological Field 129**
Parnashabari Sarkar, Sourav Sutradhar, and Biswa Nath Ghosh
- 14.1 Introduction 129
 - 14.2 Antimicrobial Activity 135
 - 14.2.1 Schiff Bases Against Gram-Positive Bacteria 135
 - 14.2.2 Schiff Bases Against Gram-Negative Bacteria 137
 - 14.3 Antifungal Activity of Schiff Bases 138
 - 14.4 Anticancer Activity of Schiff Bases and Their Metal Complexes 139
 - 14.4.1 In Vitro Activity 139
 - 14.4.2 In Vivo Activity 140
 - 14.5 Antidyslipidemic and Antioxidant Activity 141
 - 14.6 Anthelmintic Activity 141
 - 14.7 Antitubercular Activity 142
 - 14.8 Antidepressant Activity 142
 - 14.9 Anticonvulsant Activity 142
 - 14.10 Antioxidant Activity 142
 - 14.11 Antiviral Activity 143
 - 14.12 Anti-inflammatory and Analgesic Activities 143
 - References 143
- 15 Application as Catalyst 149**
Saravanan Saranya and Seenuvasan Vedachalam
- 15.1 Introduction 149
 - 15.2 Coupling Reaction 149
 - 15.3 Polymerization Reaction 151
 - 15.4 Oxidation Reaction 152
 - 15.5 Epoxidation Reaction 153
 - 15.6 Ring-Opening Epoxidation Reaction 154
 - 15.7 Cyclopropanation Reaction 155
 - 15.8 Hydrosilylation Reaction 156
 - 15.9 Hydrogenation Reaction 157
 - 15.10 Aldol Reaction 158
 - 15.11 Michael Addition Reaction 159
 - 15.12 Annulation Reaction 160
 - 15.13 Diels–Alder Reaction 161
 - 15.14 Click Reaction 161
 - 15.15 Mannich Reaction 162
 - 15.16 Ene Reaction 163
 - 15.17 Summary 164
 - References 164
- 16 Application as Drug-Delivery System 169**
Anmol Singh, Himadri Priya Gogoi, and Pranjit Barman
- References 173

17	Chemosensors/Bioimaging Applications	179
	<i>K. Sekar, K. Suganya Devi, T. Dheepa, and P. Srinivasan</i>	
17.1	Introduction	179
17.1.1	Chemosensing	179
17.1.1.1	Explosives Sensing	179
17.1.1.2	Oxygen Sensing	180
17.1.1.3	High pH Sensing	180
17.1.1.4	Other Porphyrinoid-based Chemosensors and Chemodosimeters	180
17.1.1.5	Metal Sensing	180
17.2	Chemosensors	181
17.2.1	Fluorescence ON-OFF	184
17.2.1.1	Tiny Molecules Chemosensors	184
17.2.1.2	Supramolecular Chemosensors	184
17.2.1.3	QDs-based Chemosensors	184
17.2.1.4	Fluorescent Nanomaterial-based Chemosensors	185
17.2.2	OFF-ON Chemosensors	185
17.2.2.1	Rhodamine-based Sensors	185
17.2.2.2	Coumarin-based Sensors	186
17.2.2.3	BODIPY-based Sensors	186
17.2.3	Ratiometric Fluorescent Chemosensors	186
17.2.3.1	Pyrene-based Chemosensors	186
17.2.3.2	Fluorophore Hybridization Chemosensors	186
17.2.3.3	Dual-emission Fluorescent Nanoparticles	186
17.2.4	Rhodamine-based Sensors	187
17.2.4.1	Fluorescent Bioimaging of CK in HeLa cells	187
17.2.4.2	Mice Bioimaging Experiments	187
17.2.5	Fluorescent Chemosensor for AcO^- Detection	189
17.2.6	CN^- and Al^{3+} Chemosensor for Bioimaging	191
17.3	Conclusion	192
	References	192
18	Application in Industrial Field	195
	<i>M. Chakkarapani, M.A. Asha Rani, G. Saravana Ilango, and Pranjit Barman</i>	
18.1	Introduction	195
18.2	Current Status in India	198
18.3	Conclusion	199
	References	200
	Index	203