

Contents

Preface *xiii*

1	Introduction and Fundamentals of Mixed-Valence Chemistry	1
	<i>Chun Y. Liu and Miao Meng</i>	
1.1	Introduction	1
1.2	Brief History	4
1.3	Diversity of Mixed-Valence Systems – Some Examples	6
1.4	Characterization and Evaluation of Mixed-Valence Systems	12
1.4.1	Electron Paramagnetic Resonance Spectroscopy	12
1.4.2	Electrochemical Methods	13
1.4.3	Optical Analysis	14
1.5	Important Issues in Mixed-Valence Chemistry	16
1.5.1	System Transition in Mixed Valency from Localized to Delocalized	16
1.5.2	Solvent Control of Electron Transfer	17
1.6	Theoretical Background	18
1.6.1	Potential Energy Surfaces from Classical Two-State Model	18
1.6.2	Quantum Description of the Potential Energy Surfaces	20
1.6.3	Reorganization Energies	24
1.6.4	Electronic Coupling Matrix Element and the Transition Moments	26
1.6.5	The Generalized Mulliken–Hush Theory (GMH)	27
1.6.6	Analysis of IVCT Band Shape	28
1.6.7	Rate Constant Expressions of Electron Transfer Reaction – The Marcus Theory	30
1.6.8	McConnell Superexchange Mechanism and the CNS Model	32
1.7	Conclusion and Outlook	35
	Acknowledgments	35
	References	36

2	Conceptual Understanding of Mixed-Valence Compounds and Its Extension to General Stereoisomerism	45
	<i>Jeffrey R. Reimers and Laura K. McKemmish</i>	
2.1	Introduction	45
2.2	Modeling MV and Related Chemistry	47
2.2.1	Origins Within Chemical Bonding Theory	47
2.2.2	Coupled Harmonic Oscillator Model	48
2.2.3	Intermolecular and Intramolecular Contributions to the Reorganization Energy	55
2.2.4	Effects of Electric Fields on MV Optical Band Shapes	56
2.2.5	Non-adiabatic Effects	58
2.2.6	MV Complexes as Potential Quantum Qubits	60
2.2.7	Entanglement as a Measure of the Failure of the BO Approximation	64
2.2.8	Further Reading	65
2.3	Some Traditional Mixed-Valence Example Molecules and Iconic Model Systems	65
2.3.1	Photochemical Charge Separation	66
2.3.2	MV Excited States in a Bis-Metal Complex	66
2.3.3	Hole Transport in a Molecular Conducting Material	68
2.3.4	Ground-State Delocalization in the Creutz-Taube Ion	68
2.3.5	Photochemical Charge Separation During Bacterial Photosynthesis	70
2.3.6	Prussian Blue	73
2.4	Applications to Stereoisomerism	73
2.4.1	Breakdown of Aromaticity in the $(\pi, \pi^*)^3 A_1$ Triplet Ground State of Pyridine	74
2.4.2	Isomerism of BNB	75
2.4.3	Isomerism of Ammonia and Related Molecules	75
2.4.4	Proton Transfer in $[\text{NH}_3 \cdot \text{H} \cdot \text{NH}_3]^+$	79
2.4.5	Aromaticity in Benzene	80
2.5	Conclusion and Outlook	81
	References	82
3	Quantum Chemical Approaches to Treat Mixed-Valence Systems Realistically for Delocalized and Localized Situations	93
	<i>Martin Kaupp</i>	
3.1	Introduction and Scope	93
3.2	How Did We Start	94
3.3	Moving to Transition Metal MV Systems, Getting into Conformational Aspects	97
3.4	More Recent Work on Organic MV Systems and More General Use for Charge Transfer Questions	99
3.5	More Recent Insights into Conformational Aspects for Transition Metal Complexes	100
3.6	Other Applications to Organometallic MV Systems	103

- 3.7 Limitations of the Simple Computational Protocols, Gas-Phase Benchmarks, and Improved Electronic Structure Methods 104
- 3.8 More Advanced Treatments of Environmental Effects 109
- 3.9 Conclusion and Outlook 111
- Acknowledgement 112
- References 113
- 4 Mixed Valency in Ligand-Bridged Diruthenium Complexes 121**
- Sanchaita Dey, Sudip Kumar Bera, Wolfgang Kaim, and Goutam Kumar Lahiri*
- 4.1 Introduction 121
- 4.2 Ru^{II}Ru^{III} Mixed-Valent Systems 124
- 4.2.1 Pyrazine-Derived Bridges 124
- 4.2.2 Other Bridging Ligands 130
- 4.3 Ru^{III}Ru^{IV} Mixed-Valent Systems 135
- 4.4 Ru^{II}Ru^I and Ru^IRu⁰ Mixed-Valent Systems 139
- 4.5 Conclusion and Outlook 141
- Acknowledgment 142
- References 142
- 5 Electronic Communication in Mixed-Valence (MV) Ethynyl, Butadiynediyl, and Polyynediyl Complexes of Iron, Ruthenium, and Other Late Transition Metals 151**
- Sheng Hua Liu, Ya-Ping Ou, and František Hartl*
- 5.1 Introduction 151
- 5.2 Iron–Ethynyl Complexes 152
- 5.2.1 Dinuclear Iron–Ethynyl Complexes with Butadiynediyl Bridge 153
- 5.2.2 Dinuclear Iron–Ethynyl Complexes with Diynediyl, Polycyclic Aromatic Hydrocarbons and Heterocycles in the C₄ Bridge Core 154
- 5.2.3 Dinuclear Iron–Ethynyl Complexes with Non-conjugated C₄ Bridge Core 156
- 5.2.4 Functionalized Dinuclear Iron–Ethynyl Complexes 157
- 5.3 Ruthenium–Ethynyl Complexes 158
- 5.3.1 Dinuclear Ruthenium–Ethynyl Complexes with Cp'(L₂)Ru-Based Termini 158
- 5.3.2 Dinuclear Ruthenium–Ethynyl Complexes with Ru(dppe)₂X-Based Termini 163
- 5.3.3 Ruthenium–Ethynyl Complexes with Alternating Polyynediyl and Capped Ru–Ru Units 165
- 5.3.4 Ruthenium–Ethynyl Complexes with Other Ruthenium–Ethynyl Termini and Core Units 166
- 5.4 Other Transition Metal–Ethynyl Complexes 168
- 5.4.1 Dinuclear Group 6 (Cr and Mo) Metal–Ethynyl Complexes 168

5.4.2	Dinuclear Group 7 (Mn and Re) Metal–Polyynediyl Complexes	169
5.4.3	Dinuclear Group 8 (Os) and Group 9 (Co) Metal–Polyynediyl Complexes	170
5.5	Concluding Remarks and Outlook	171
	Acknowledgment	172
	References	172
6	Electron Transfer in Mixed-Valence Ferrocenyl-Functionalized Five- and Six-Membered Heterocycles	181
	<i>Peter Frenzel and Heinrich Lang</i>	
6.1	Introduction	181
6.2	Ferrocenyl-Functionalized Five-Membered Heterocycles	182
6.2.1	Five-Membered Heterocyclic Compounds with Group 13 Elements	183
6.2.2	Five-Membered Heterocyclic Compounds with Group 14 Elements	183
6.2.3	Five-Membered Heterocyclic Compounds with Group 15 Elements	185
6.2.4	Five-Membered Heterocyclic Compounds with Group 16 Elements	201
6.2.5	Five-Membered Heterocyclic Compounds with Transition Metal Elements	213
6.3	Ferrocenyl-Functionalized Six-Membered Heterocycles	217
6.4	Conclusion and Outlook	218
	Acknowledgment	219
	References	220
7	Electronic Coupling and Electron Transfer in Mixed-Valence Systems with Covalently Bonded Dimetal Units	229
	<i>Chun Y. Liu, Nathan J. Patmore, and Miao Meng</i>	
7.1	Introduction	229
7.2	Synthesis and Characterization	233
7.3	$d(\delta)(M_2)-p(\pi)(\text{Ligand})$ Conjugation	235
7.4	Electronic and Intervalence Transitions and DFT Calculations	238
7.5	Transition in Mixed Valency Between Robin–Day Classes	240
7.6	Distance Dependence of Electronic Coupling and Electron Transfer	247
7.7	Conformational Effects of Electronic Coupling and Electron Transfer	252
7.8	Class III and Beyond	256
7.9	Cross-Conjugation and Quantum Destructive Effect	257
7.10	Electronic Coupling and Electron Transfer Across Hydrogen Bonds	258
7.11	Mixed-Valence Diruthenium Dimers	260
7.12	Conclusions and Outlook	262
	Acknowledgments	263
	References	263

- 8 Mixed-Valence Electron Transfer of Cyanide-Bridged Multimetallic Systems 269**
Shao-Dong Su, Xin-Tao Wu, and Tian-Lu Sheng
- 8.1 Introduction 269
- 8.2 Dinuclear Cyanide-Bridged Mixed-Valence Complex 272
- 8.3 Trinuclear Cyanide-Bridged Mixed-Valence Complex 276
- 8.4 Tetranuclear and Higher Nuclear Cyanide-Bridged Mixed-Valence Complex 284
- 8.5 Conclusion and Outlook 290
Acknowledgment 290
References 291
- 9 Organic Mixed-Valence Systems: Toward Fundamental Understanding of Charge/Spin Transfer Materials 297**
Akihiro Ito
- 9.1 A Brief Sketch of the History of Organic Mixed-Valence Systems 297
- 9.2 A Glossary for This Chapter 299
- 9.2.1 Hush Analysis 300
- 9.2.2 Mulliken–Hush Two-State Analysis 301
- 9.2.3 Mulliken–Hush Two-Mode Analysis 301
- 9.2.4 Generalized Mulliken–Hush Three-State Analysis 302
- 9.3 Relationship Between Bridging Units and Electronic Coupling 304
- 9.4 Where to Attach Redox Centers 310
- 9.5 Through-Bond or Through-Space? 311
- 9.6 Control of Spin States Through Mixed-Valence States 314
- 9.7 Future Prospects 315
Acknowledgment 316
References 316
- 10 Mixed-Valence Complexes in Biological and Bio-mimic Systems 323**
Xiangmei Kong, Yixin Guo, Zijie Zhou, and Tianfei Liu
- 10.1 Introduction 323
- 10.2 Mixed-Valence Iron–Sulfur Clusters in Biological and Bio-mimic Systems 325
- 10.2.1 Basic FeS Clusters 325
- 10.2.2 [FeFe]-Hydrogenase 326
- 10.2.3 Nitrogenases 328
- 10.2.4 Carbon Monoxide Dehydrogenase 329
- 10.3 Mixed-Valence Systems in Multiheme and Other Multiiron-Contained Biological Systems and Their Mimics 331

- 10.4 Mixed-Valence Multicopper Cofactors in Biological and Mimicking Systems 332
- 10.5 OEC and Other Mixed-Valence Multimanganese Cofactors 336
- 10.6 Summary 339
 - Acknowledgement 339
 - References 340

- 11 Control of Electron Coupling and Electron Transfer Through Non-covalent Interactions in Mixed-Valence Systems 349**
Zijie Zhou, Yixin Guo, Xiangmei Kong, Ying Wang, and Tianfei Liu
- 11.1 Introduction 349
- 11.2 Electronic Coupling Through Hydrogen Bonds 350
 - 11.2.1 Electronic Coupling Between Transition Metal Centers Through Hydrogen Bonds 350
 - 11.2.2 Electronic Coupling Between Organic Fragments Through Hydrogen Bonds 353
- 11.3 Modulation of Electronic Coupling via Host–Guest or Through-Space Interaction 356
- 11.4 Conclusion 361
 - Acknowledgment 361
 - References 361

- 12 Stimulus-Responsive Mixed-Valence and Related Donor–Acceptor Systems 365**
Jiang-Yang Shao and Yu-Wu Zhong
- 12.1 Introduction 365
- 12.2 Photoswitchable Compounds 365
- 12.3 Anion-Responsive Compounds 378
- 12.4 Proton-Responsive Compounds 380
- 12.5 Conclusion and Outlook 385
 - Acknowledgement 385
 - References 385

- 13 Mixed Valency in Extended Materials 393**
Harrison S. Moore, Eleanor R. Kearns, Martin P. van Koevorden, and Deanna M. D'Alessandro
- 13.1 Introduction 393
 - 13.1.1 Fundamental Aspects of Mixed Valency in the Solid State 393
 - 13.1.2 Quantum Mechanical Considerations in Mixed Valency and IVCT 394
 - 13.1.3 Marcus–Hush Theory and the Quantification of CT 395
 - 13.1.4 Classifications of Mixed Valency 395
 - 13.1.5 Organic Mixed Valency 396
- 13.2 Electron Transfer in Extended MV Materials 397
 - 13.2.1 Introduction to Extended Materials 397
 - 13.2.2 Organic-Based Mixed Valency in Extended Frameworks 397

13.2.2.1	Thiazolo[5,4- <i>d</i>]thiazole-Based Compounds	397
13.2.2.2	Tetrathiafulvalene (TTF)-Based Compounds	399
13.2.2.3	Tetraoxolene-Based Compounds	400
13.2.2.4	Naphthalenediimide (NDI)-Based Compounds	405
13.2.2.5	Phenalenyl-Based Compounds	406
13.2.2.6	Covalent-Organic Frameworks (COFs)	407
13.2.3	Metal-Based Mixed Valency	408
13.2.3.1	First-Row Transition Metals	408
13.2.3.2	Other Metals	414
13.2.3.3	Catalysis in Uncoupled MV Systems	414
13.3	Conclusion	418
	References	419
14	Near-Infrared Electrochromism Based on Intervalence Charge Transfer	431
	<i>Ying Han, Xiaohua Cheng, Yu-Wu Zhong, and Bin-Bin Cui</i>	
14.1	Introduction	431
14.2	Near-Infrared Electrochromic Materials	432
14.2.1	Inorganic NIR Electrochromic Materials	433
14.2.2	Organic NIR Electrochromic Materials	435
14.2.2.1	Viologen Derivatives	435
14.2.2.2	Triphenylamine Derivatives	437
14.2.2.3	Organic Conducting Polymers	439
14.2.2.4	Covalence-Organic Framework (COF)	442
14.2.3	Organic-Inorganic Hybrid NIR Electrochromic Materials	444
14.2.3.1	Metal Complexes	444
14.2.3.2	Conducting Polymers of Metal Complexes	447
14.2.3.3	Monolayer and Multilayer Assembled Films	452
14.3	Potential Applications of NIR Electrochromic Materials	453
14.3.1	Smart Windows	453
14.3.2	Molecular Logic Gates and Optical Storage	453
14.3.3	Optical Communication	453
14.3.4	Military Camouflage	454
14.4	Summary and Outlook	454
	Acknowledgment	455
	References	455
15	Manipulation of Metal-to-Metal Charge Transfer Toward Switchable Functions	463
	<i>Wen Wen, Yin-Shan Meng, and Tao Liu</i>	
15.1	Introduction	463
15.2	Switchable Cyanide-Bridged MMCT Systems	465
15.3	Cyanide-Bridged MMCT Complexes Showing Switchable Functional Properties	472
15.3.1	Modulating Molecular Nanomagnet Behavior	472

15.3.2	Modulating Molecular Electric Dipole	474
15.3.3	Modulating Thermal Expansion Behavior	478
15.3.4	Modulating Photochromic Behavior	480
15.4	Conclusion and Outlook	483
	References	484

Index	492
--------------	-----