Ram Charitra Maurya

Bioinorganic Chemistry

Some New Facets

Contents

Preface — VII

Cha	pter	ı
-----	------	---

Coordination chemistry of chlorophylls/bacteriochlorophylls and its
functional aspects in photosynthesis — 1

1.1	Introduction —— 1
1.2	Diverse photosynthetic organisms —— 2
1.2.1	Photosynthetic organisms: dependence on different hydrogen
	donors — 3
1.3	Light and dark reactions in photosynthesis — 4
1.3.1	Photo-phase or light reaction —— 5
1.3.2	Synthesis-phase or dark reactions — 5
1.4	Chloroplasts: the photosynthesis location — 7
1.5	Light-harvesting pigments: chlorophylls —— 8
1.5.1	Accessory pigments in thylakoids (photosynthetic cells) — 10
1.6	Chlorophylls in photosynthetic light absorption: absorption
	spectra of various photosynthetic pigments and their
	functions —— 13
1.7	The role of Mg(II) in chlorophylls —— 16
1.8	Hill reactions: illuminated chloroplasts evolve O ₂ and reduce
	electron acceptors —— 17
1.9	Photosystems I and II in photosynthesis by green plants —— 19
1.9.1	Red drop —— 20
1.9.2	Photosystem I (also called PS-I or P-700, P stands for
	pigment) —— 21
1.9.3	Photosystem II (abbreviated as PS-II or P-680) —— 21
1.9.4	Photosystem I —— 21
1.9.5	Water splitting reactions assisted by a water splitting complex
	(Mn ₄ cluster) —— 23
1.9.6	Dark reaction —— 27
1.9.7	Cyclic photophosphorylation in photosynthesis —— 27
1.10	Antenna chlorophylls and reaction centres in chloroplasts —— 28
	Reference —— 30
	Exercises —— 30

Chapter II

Complexes containing nitric oxide: synthesis, reactivity, structure, bonding and therapeutic aspects of nitric oxide-releasing molecules (NORMs) in human beings and plants —— 35

2.1	Introduction —— 35
2.1.1	Discovery of nitric oxide (NO) —— 35
2.1.2	Importance of nitric oxide complexes —— 35
2.2	Metal nitrosyl complexes? —— 37
2.3	Synthetic methods of metal nitrosyls —— 38
2.3.1	Nitric oxide gas as the nitrosylating agent — 38
2.3.2	NO ⁺ as the nitrosylating agent —— 42
2.3.3	Nitrosyl halide (NOX) as the nitrosylating agent —— 43
2.3.4	N-Nitrosoamides as the nitrosylating agents —— 45
2.3.5	Coordinated NO as the nitrosylating agents — 46
2.3.6	Hydroxylamine (NH ₂ OH) as the nitrosylating agents — 46
2.3.7	Acidic solution of nitrite salts (NO_2^-/H^+) as the nitrosylating
	agents 49
2.3.8	Alkyl nitrites as the nitrosylating agents —— 50
2.3.9	Nitric acid as the nitrosylating agent —— 50
2.3.10	Synthesis of nitrosyl complexes using redox reaction —— 51
2.3.11	Synthesis of metal nitrosyl by substitution of cyano groups in
	parent cyanonitrosyl complex —— 52
2.4	The $\{M(NO)_m\}^n$ formalism for metal nitrosyl complexes — 52
2.4.1	Limitations of the $\{M(NO)_m\}^n$ formalism —— 54
2.5	Alternative formalism/notation for metal nitrosyl complexes —— 55
2.6	Simplified procedure for calculation of EAN of metal nitrosyl
	complexes — 60
2.7	New notation with the formal charges on the nitrosyl ligand and
	the formal metal oxidation state —— 61
2.8	Transition metal nitrosyl complexes: bonding —— 62
2.8.1	Structural studies: X-ray study —— 62
2.8.2	M.O. calculations of bonding in metal nitrosyls: linear to bent
	MNO bond angle transformation in hexa- and penta-coordinated
	nitric oxide complexes — 72
2.8.3	Molecular orbital calculations: density functional theory
	approach — 77
2.8.4	Linear versus bent nitrosyl ligands: Enemark–Feltham
	approach — 79
2.9	Characterization of metal nitrosyl complexes using spectroscopic
	and other physical methods —— 83
2.9.1	Vibrational spectral studies — 83
2.9.2	Electronic spectral studies — 89

2.9.3	Magnetic properties —— 97
2.9.4	Electron spin resonance (ESR) studies —— 101
2.9.5	Nuclear magnetic resonance (NMR) spectral studies — 106
2.9.6	X-ray photoelectron spectroscopy or ESCA studies —— 107
2.9.7	Mössbauer (MB) spectral studies —— 110
2.9.8	Kinetic studies —— 115
2.9.9	Nuclear resonance vibrational spectroscopic studies —— 117
2.9.10	Mass spectral studies —— 118
2.10	Reactivity of nitric oxide coordinated to transition metals —— 121
2.10.1	Nucleophilic attack —— 123
2.10.2	Electrophilic attack of coordinated NO —— 125
2.10.3	Reduction reactions —— 126
2.10.4	Oxygenation reactions in metal nitrosyls —— 127
2.11	Other reactions — 129
2.11.1	Nitric oxide (NO): insertion reactions —— 129
2.11.2	Transfer of coordinated NO to the other metals —— 129
2.12	Transition metal nitrosyls: organic synthesis and in pollution
	control —— 130
2.12.1	Transition metal nitrosyls: organic synthesis —— 130
2.12.2	Coordinated NO group: some reactions —— 135
2.12.3	Metal nitrosyls as depolluting agents —— 136
2.13	Applications of metal nitrosyls —— 141
2.13.1	Biomedical science —— 142
2.14	NO news is good news for eyes: NO donors for the treatment of
	eye diseases —— 166
2.14.1	Biosynthesis of nitric oxide —— 167
2.14.2	Roles of nitric oxide in eyes —— 168
2.14.3	Use of NORMs in the treatment of eye defects —— 170
2.14.4	Mechanism of action of NO in IOP lowering —— 176
2.15	Role of NO and exogenous NO donors in plants —— 177
2.15.1	Biosynthesis of nitric oxide —— 177
2.15.2	Nitric oxide action in plants —— 179
2.16	Conclusions —— 186
	References —— 186

Exercises —— 198

Chapter III

Complexes containing carbon monoxide: synthesis, reactivity, structure, bonding and therapeutic aspects of carbon monoxide-releasing molecules (CORMs) in human beings and plants —— 205

(CORMS) II	n numan beings and plants —— 205
3.1	Introduction —— 205
3.2	Metal carbonyls —— 206
3.3	Synthesis of metal carbonyls —— 207
3.4	Physical properties —— 211
3.5	Chemical properties/reactivity of metal carbonyls —— 211
3.5.1	Displacement or substitution reactions —— 211
3.5.2	Formation of cationic carbonyl complexes: carbonylate
	cations —— 212
3.5.3	Formation of anionic carbonyl complexes: carbonylate anions —— 213
3.5.4	Redox reactions including the formation and cleavage of metal-
	metal bonds —— 214
3.5.5	Reaction with NO —— 214
3.5.6	Action of heat —— 214
3.5.7	Insertion reactions —— 215
3.5.8	Nucleophilic attack on coordinated CO —— 216
3.5.9	Electrophilic addition to the carbonyl oxygen —— 217
3.5.10	Disproportionation reaction —— 217
3.5.11	Collman's reagent —— 217
3.5.12	Oxidative decarbonylation —— 218
3.5.13	Photochemical substitution —— 218
3.6	Catalytic aspect of metal carbonyls —— 219
3.6.1	Hydrogenation of alkenes —— 219
3.6.2	Hydroformylation reaction —— 221
3.6.3	Manufacturing of CH ₃ COOH by carbonylation of CH ₃ OH using
	metal carbonyl as catalyst —— 224
3.6.4	Manufacturing of acetic anhydride by carbonylation of
	CH₃COOCH₃ — 228
3.6.5	Importance of acetic anhydride —— 229
3.6.6	Manufacturing of acetic acid by BP Cativa process using iridium
	carbonyl as a catalyst —— 230
3.6.7	Carbonylation of olefins and acetylenes to carboxylic acids or
	esters or alcohols using metal carbonyls as a catalyst —— 231
3.7	Metal carbonyls: effective atomic number (EAN) rule —— 233
3.7.1	Mononuclear carbonyls having metallic atom with even atomic
	numbers —— 234
3.7.2	Mononuclear carbonyls having metallic atom with odd atomic
	numbers —— 234

3.7.3	Polynuclear carbonyls —— 235
3.7.4	Utility of EAN rule —— 238
3.8	Eighteen-electron rule for metal carbonyls — 240
3.8.1	Eighteen-electron rule: square planar complexes — 244
3.9	Types of bond present in metal carbonyls —— 245
3.10	Structure of metal carbonyls: valence bond (VB) approach — 247
3.11	Bonding in metal carbonyls: nature of M–C and C–O bonds in metal carbonyls —— 261
3.11.1	Formation of OC \longrightarrow M σ -bond: valence bond theory (VBT) approach \longrightarrow 262
3.11.2	Formation of OC \longrightarrow M σ -bond and M \longrightarrow CO π bond: molecular
J	orbital theory (MOT) approach —— 263
3.11.3	Bonding in metal carbonyl versus π-complexes of unsaturated
	organic ligands —— 265
3.11.4	Metal carbonyls and IR spectra —— 265
3.12	Metal carbonyl compounds: a new class of
	metallopharmaceuticals —— 270
3.12.1	Introduction —— 270
3.12.2	Sources of CO in the human body —— 271
3.12.3	Generated CO in mammals: target sites —— 274
3.13	CO signalling in anti-inflammatory responses — 277
3.14	Therapeutic scope of CO —— 279
3.14.1	Ways of CO delivery in human body as a therapeutic agent —— 279
3.14.2	Requirement of exogenous endeavour, why? —— 281
3.15	Therapeutic applications of CO and CO resealing molecules/materials —— 282
3.15.1	Role of exogenously applied CO gas —— 283
3.15.2	Carbon monoxide-releasing molecules (CORMs) and photoactive
	CORMs or photoCORMs —— 285
3.16	CO as a signalling molecule in plants:
	a vegetation echo of CO — 297
3.16.1	Introduction —— 297
3.16.2	Synthesis of CO in plants —— 298
3.16.3	Role of CO in plant growth and development — 299
3.16.4	Role of CO in abiotic stresses —— 303
3.17	Cross-talk between CO and other signalling molecules —— 305
3.17.1	Cross-talk between CO and NO —— 306
3.17.2	Cross-talk between CO and phytohormone —— 307
3.17.3	Cross-talk between CO and other small signalling molecules —— 307

3.18 Concluding remarks —— 308
References —— 309
Exercises —— 318

Chapter IV

Advantageous role of gaseous signalling molecule, $\rm H_2S$: hydrogen sulphide and their respective donors, in ophthalmic diseases and physiological implications in plants —— 325

implication	5 in plants 325
4.1	Introduction —— 325
4.2	Introductory view of gasotransmitters: endogenous signalling
	molecules —— 327
4.3	Biosynthesis of H ₂ S — 328
4.3.1	In ocular tissues —— 328
4.3.2	In plants —— 330
4.4	Biological chemistry of H ₂ S —— 331
4.5	Implications of H ₂ S in ophthalmic diseases —— 333
4.5.1	Introduction —— 333
4.5.2	Ocular drug delivery —— 334
4.5.3	Ocular bioavailability —— 334
4.5.4	H ₂ S and glaucoma —— 336
4.5.5	H ₂ S and diabetic retinopathy —— 339
4.5.6	H ₂ S and retinal degeneration — 342
4.6	Physiological functions of H ₂ S in plants —— 343
4.6.1	Introduction —— 343
4.6.2	Improvement in seed germination and plant growth —— 344
4.6.3	H ₂ S in fruit ripening and post-harvest damage to fresh
	produce —— 345
4.6.4	Abiotic stresses in plants —— 345
4.6.5	Crop plants and biotic stress — 349
4.6.6	Exogenously applied NaHS: activation of H ₂ S signalling — 349
4.6.7	Cross-adaptation: persuaded by H ₂ S —— 350
4.7	Conclusions — 354
	References —— 354
	Exercises —— 363

Appendix I

The International System of Units, fundamental physical constants and conversion factors —— 367

Appendix II

Body mass index (BMI): an indicator of our body fat --- 373

Appendix III

Amino acids, the building blocks of proteins: names, symbols, structures, properties and some physical constants —— 375

Bibliography --- 387

Index ---- 391