Contents

Preface v

Preface to English Edition vii

List of Abbreviations ix

1 General Concepts of Porphyrin and Phthalocyanine Complexes . . 1
- 1.1 Specific Features of Natural and Synthetic Porphyrin Complexes 1
- 1.2 Metalloporphyrins in Biological Systems. Industrial Uses of Phthalocyanine Complexes 4
- 1.3 The Role of Complexing in the Formation, Dissociation, and Functioning of Metalloporphyrin Systems 9

2 Synthesis, Isolation, and Purification of Porphyrin and Phthalocyanine Complexes 11
- 2.1 Isolation of Porphyrin Complexes (Chlorophyll, Haemin) and the Corresponding Porphyrins from Natural Sources . . 11
- 2.2 Synthesis of Complexes of Various Porphyrins 13
- 2.3 Synthesis of Spectroscopically Pure Phthalocyanine, Polymeric Phthalocyanine, and Their Complexes 17

3 Molecular Structure of Porphyrins and Phthalocyanine 23
- 3.1 Aromatic Nature of Porphyrins 23
- 3.2 Structural Features of Phthalocyanine and Porphyrin Molecules 26
- 3.3 Quantum-chemical Data on the Structure of Porphyrins and Phthalocyanine 36

4 Ionization and Coordination Properties of Porphyrins and Phthalocyanine 39

IONIZATION PROPERTIES

4.1 Acid Dissociation of Porphyrins and Phthalocyanine . . . 40
4.2 The State of Porphyrin and Phthalocyanine Molecules in Proton-donor Media 59
4.3 Thermodynamics of Acid–Base Interaction of Phthalocyanine and Porphyrin Complexes 66
4.4 Enthalpy–Entropy Characteristics of Processes of Protolytic Dissolution and Protonation of Phthalocyanine Complexes . 76

COORDINATION PROPERTIES

4.5 Electronic Effects of Coordination 80
4.6 Kinetics of Formation of Chlorophyll and Its Metal Analogues in Organic Solvents 84
4.7 Kinetics of Formation of Haemin and Its Analogues in Solution 103
4.8 Reactivity of Other Porphyrins in Coordination Reactions . . 106
4.9 Mechanism of Formation of Metalloporphyrins in Solution . 120
4.10 The Role of Acid–Base Interaction in Complexing Reactions . 131

5 The Kinetics and Mechanism of Protolytic Dissociation of Porphyrin and Phthalocyanine Complexes 135
5.1 Dissociation of Phthalocyanine Complexes and Their Polymers in Proton-donor Media 135
5.2 Dissociation of Chlorophyll, Haemin, and Their Analogues . 144
5.3 Influence of the Solvent on Dissociation 169
5.4 Metalloporphyrin Dissociation Mechanism 175
5.5 Kinetic Criterion of Stability of Porphyrin and Phthalocyanine Complexes 183

6 Thermodynamics of Porphyrin and Phthalocyanine Complex Formation 189
6.1 Results of Direct Equilibrium Measurements 189
6.2 Calculation of Equilibrium Constants from Kinetic Data . . 191
6.3 Stability Series. Factors Responsible for High Stability of Macrocyclic Complexes 194
6.4 Extra Coordination in Porphyrin Complexes 199

7 Electron-optical Properties and Their Correlation with Other Properties of Porphyrin and Phthalocyanine Complexes 209
7.1 On the Origin of Bands in Electronic Absorption Spectra of Porphyrins and Their Complexes 209
7.2 Manifestation of Ionization and Coordination Properties of Porphyrins in Absorption Spectra 214

7.3 Spectral Criterion of Stability of Porphyrin and Phthalocyanine Complexes 219
7.4 Spectral Data on the Cyclopentanone Ring of Chlorophyllic Acid and Its Complexes 225
7.5 Spectral Manifestations of Association of Porphyrins in Solution 228
7.6 Polymeric State of Phthalocyanine and Its Optical Properties 233

8 Other Properties of Metalloporphyrins 237
8.1 Photochemical Stability of Chlorophyll and Its Metal Analogues in Solution 237
8.2 Oxidation–Reduction Reactions 242
8.3 Catalytic Activity 249
8.4 Semiconductor Properties of Phthalocyanine Complexes . . 255

Conclusion 259

References 265

Index 281