

## Contents

<b>Preface</b>	v
<b>Preface to English Edition</b>	vii
<b>List of Abbreviations</b>	ix
<b>1 General Concepts of Porphyrin and Phthalocyanine Complexes</b>	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
<b>2 Synthesis, Isolation, and Purification of Porphyrin and Phthalocyanine Complexes</b>	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
<b>3 Molecular Structure of Porphyrins and Phthalocyanine</b>	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
<b>4 Ionization and Coordination Properties of Porphyrins and Phthalocyanine</b>	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
<b>5</b>	<b>The Kinetics and Mechanism of Protolytic Dissociation of Porphyrin and Phthalocyanine Complexes . . . . .</b>	<b>135</b>
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
<b>6</b>	<b>Thermodynamics of Porphyrin and Phthalocyanine Complex Formation . . . . .</b>	<b>189</b>
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
<b>7</b>	<b>Electron-optical Properties and Their Correlation with Other Properties of Porphyrin and Phthalocyanine Complexes . . . . .</b>	<b>209</b>
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
<b>8</b>	<b>Other Properties of Metalloporphyrins</b> . . . . .	<b>237</b>
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
<b>Conclusion</b> . . . . .		<b>259</b>
<b>References</b> . . . . .		<b>265</b>
<b>Index</b> . . . . .		<b>281</b>

the four equivalent, or almost equivalent, coordination donor-acceptor sites. If the interaction between the metal and the porphyrin cation is purely electrostatic, labile ion complexes are formed. These include complexes of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Be}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ , and some other cations. But if the electrostatic interaction involves filling of the vacant orbitals of the central atom by the electrons of the donor N atoms of the ligand, stable porphyrin complexes of the covalent or predominantly covalent type are formed. In this case we have complexes of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Ge}^{4+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{V}^{4+}$ ,  $\text{P}^{5+}$ ,  $\text{O}^{6+}$ , and other cations. Most of the above complexes are formed by biometals. As will be seen from what follows, complexes of porphyrins with  $\text{Mn}^{2+}$  that is chlorophyll and its structural analogues, do not belong either to purely ionic complexes or to the stable group of predominantly covalent complexes. This peculiarity of chlorophyll, stemming from its intermediate position in the complex stability series, is to some extent responsible for its unique role in nature.

In contrast to chlorophyll, the complex of protoporphyrin with  $\text{Fe}^{2+}$  ( $\text{Fe}^{3+}$ ) is one of the most stable metalloporphyrins of the covalent type. This property is fully consistent with both the biological composition of the medium in which heme acts as a complex with protein and with its biological functions.

The specific features of metalloporphyrins as intercomplex compounds are due not only to the polydentate (tetradentate) nature of the ligand but also to its rigidity. The latter is determined by the planar structure of the large ring of the porphyrin molecule, by the unique conjugation in it which