67 Porphyrinoids

67.1 Porphyrins and Phthalocyanines as Polyaza[18]annulenes

Porphyrinoids comprise porphyrins (from Greek porphyrus = purple) of natural origin and synthetically obtained phthalocyanines including their metal chelates. They represent polyaza[18]annulenes.

Four pyrrole rings linked with methine groups at the α,α′-positions make up the parent macrocyclic porphyrin ring system called porphine. Following the red bonds in the tautomers given, porphyrins (X = CH) and their metal chelates turn out to be diaza[18]annulenes. Four imino nitrogen atoms replace the methine fragments in the benzo-fused phthalocyanine. Once more tracking the red bonds in the formulas, phthalocyanines (X = N) and their metal chelates can be considered as hexaza[18]annulenes.

To conclude, planar porphyrins and phthalocyanines have 18 electron & Hückel’s (4N + 2) rule with N = 4 as a criterion for aromaticity (Chapters 23.3, 29.1). Metal-free porphyrins exist as tautomers in which diagonal ring nitrogen atoms exchange their hydrogen atoms.

The outstandingly intense Soret band (λmax ~ 410 nm) in the electronic spectra (Chapter 66.1) of porphyrins and longer-wavelength maxima (λmax > 500 nm) are attributed to the tetrameric push-pull system of 3-aminoacrolein imine present in the porphyrin ring.

As tetradeutate ligands with four nitrogen donors (N₄ ligands), porphyrins and phthalocyanines chelate metal cations with ionic radii of about 70 pm (1 pm = 10⁻¹² m). Substituted phthalocyanine metal chelates, industrially prepared from phthalic acid derivatives such as phthalimide and phthalodinitrile in the presence of metal salts, are widely used as dyes, colorants, and pigments. Substituents at the benzenoid rings (Cl, SH, C₆H₅) change the color from blue to green. Red phthalocyanines contain 1,4-dithiane rings instead of benzene rings.

67.2 Porphyrinoids in Blood and Chloroplasts

67.2.1 Heme

In the protein hemoglobin (structure: Fig. 69.2 c and d) of red blood corpuscles, the ferrous chelate (chelated ion: Fe²⁺) of a substituted porphyrin called heme (from Greek kaima = blood) is the non-protein organic function. It is referred to as the prosthetic group of hemoglobin, shown in Fig. 67.1 c, not only giving the red color to the protein but, most importantly, also enabling it to carry oxygen in the breathing process. The ferrous ion is coordinated (chelated) to the four pyrrole nitrogens of the porphyrin ring and to an imidazole nitrogen of the amino acid histidine (Chapter 68.1) in the protein sequence. This fifth coordination to the so-called proximal histidine ties heme to the protein (Fig. 67.1 c). Oxygen takes the sixth coordination position of the ferrous ion of heme protected in a hydrophobic pocket of hemoglobin during transport in the blood flowing from the lungs to the muscles and other tissues where oxygen is needed. Carbon dioxide produced by "metabolic burning" of carbohydrates in the tissues reacts with N-terminal amino groups of hemoglobin to give carbamate (Chapter 55.3.2); in this state it is carried away by the protein in the blood back to the lungs where it is set free and exhaled. Stronger binding carbon monoxide ([O=C=O]⁻) and the isoelectronic cyanide anion ([C≡N]⁻) of hydrogen cyanide displace oxygen in oxygenated hemoglobin, disrupting oxygen transport, causing tachypnea, cyanosis, coma, and death.
Hot acetic acid cleaves hemoglobin. **Hemin** is the ferric chelate (chelated ion: Fe$^{3+}$) which crystallizes from the solution obtained by pouring blood into hot acetic acid containing some sodium chloride (Fig. 67.1 b). **Protoporphyrin** is the name of the metal-free ligand (Fig. 67.1 a).

![Diagram](image.png)

**Fig. 67.1.** Protoporphyrin (a), hemin (b), and tube model of heme in hemoglobin (c), attached to the helical parts (green) of the protein by coordination of the ferrous ion to the imidazole nitrogen atom of the proximal histidine (left side); oxygen takes the sixth coordination position of the ferrous ion in oxygenated hemoglobin, controlled by the distal histidine (right side).

### 67.2.2 Chlorophyll

**Chlorophyll a** (methyl) and **b** (aldehyde) are found in the chloroplasts of plants. They can be extracted from leaves with methanol or acetone, separated by chromatography on silica gel, and isolated as waxy blue-black microcrystals; the waxyness arises from the diterpenoid phytol ester residue (Chapter 76.3.3). Both chlorophylls are magnesium chelates of a substituted **chlorin**. The parent chlorin derived from porphine contains one partially hydrogenated pyrrole ring; thus, the aromatic diaza[18]annulene system is not disrupted.

![Diagram](image.png)

The **light reaction** of photosynthesis occurs in the membrane of chloroplasts where chlorophyll-protein complexes collect photons. These excite other chlorophyll molecules, inducing **photolysis of water to oxygen** by the nicotinamide coenzyme NADPH$^+$ which undergoes reduction to 1,4-dihydronicotinamide NADPH$^-$H$. The **dark reaction of photosynthesis** in the stoma of chloroplasts involves **reductive conversion of carbon dioxide into D-glucose** via D-glyceraldehyde (Chapter 71.1) by the reducing coenzyme NADPH$^-$H$. Without photosynthetically produced oxygen and D-glucose, animal and human life on earth would be impossible.

![Diagram](image.png)

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**Chapter 67 permits answers to the following:**

**67.1** How do you account for the outstanding stability of porphyrins and phthalocyanines?

**67.2** What is the difference between heme and hemin? How is hemin obtained?

**67.3** What is the difference between porphine and chlorin? Draw formulas.

**67.4** Briefly outline the biological function of (a) heme and (b) chlorophyll.