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The Isolation and Investigation of Molecular Complexes formed between Porphyrins and Aromatic Nitro-compounds

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THE possible roles played by porphyrins as electron donors in the photosynthetic process has led[1] to interest in the capacity of these molecules to form molecular complexes with possible electron acceptors. We have succeeded in isolating molecular complexes formed by aetio- and meso-porphyrin IX dimethyl ester and their cobalt(II) derivatives with a number of aromatic nitro-compounds. Previous work has indicated the existence of similar complexes in nitrobenzene[2] and in water.[3]

Treatment of a chloroform solution of cobalt(II) aetioporphyrin with an excess of 1,3,5-trinitrobenzene gave on evaporation a solid, the molecular complex contaminated with excess of trinitrobenzene. The latter could be removed by washing with cold glacial acetic acid. Complexes of cobalt(II) aetioporphyrin and 3,5-dinitrobenzonitrile, and cobalt(II) mesoporphyrin dimethyl ester and 1,3,5-trinitrobenzene were isolated in the same way. The complex formed between aetioporphyrin itself and 2,4,7-trinitrofluorenone, precipitated from glacial acetic acid. A 1 : 1 stoicheiometry for all these complexes was established by elemental analysis. Spectrophotometric investigations of the formation of these complexes in chloroform were consistent with the existence of 1 : 1 complexes in solution. For example, using the method of "continuous variation" at 500 mμ, the "Job's plot" showed a minimum at a 1 : 1 ratio of aetioporphyrin and trinitrofluorenone. The visible and u.v. spectra of all the complexes isolated, and of some others which have not yet been isolated, were recorded in chloroform as solvent at room temperature. As noted previously,[2] there is a distinct change in the intensity of the α- and

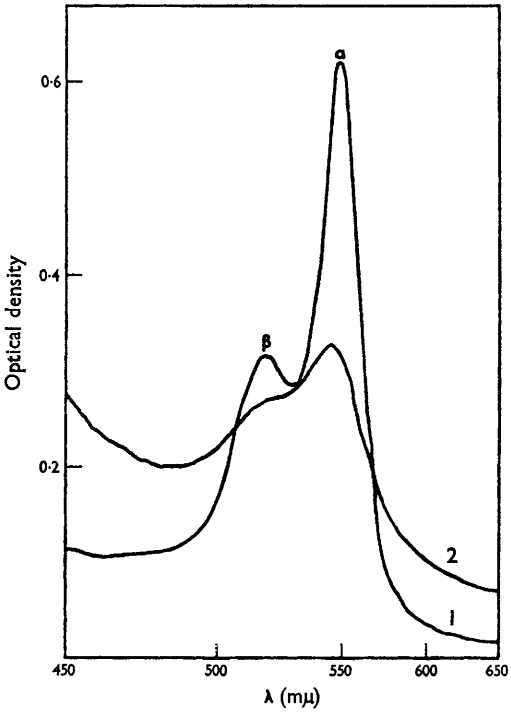

FIGURE. *Absorption spectrum of cobalt*(II) *mesoporphyrin dimethyl ester* (3 × 10^{-5} M *in chloroform*): (1) *no trinitrofluorenone*, (2) *with trinitrofluorine* (1 × 10^{-2} M).

β-bands (see the Figure). The change in intensity of the α-band of the aromatic compound was utilised in the spectrophotometric determination of the stability constant K for the equilibrium,

porphyrin + aromatic compound $\rightleftharpoons$ molecular complex,

The change in optical density of a 3×10^{-5} M solution of cobalt(II) mesoporphyrin dimethyl ester on addition of an excess of aromatic compound was measured. Plotting[4] (concentration of aromatic compound)/(change in optical density) against concentration of aromatic compound yielded the stability constant, assuming a 1 : 1 complex. K depends markedly on the "electron-affinity"[5] of the aromatic compound, *viz.*,

Aromatic compound	K (l. mole^{-1})
2,4,7-Trinitrofluorenone	2,500 ± 100
1,3,5-Trinitrobenzene	120 ± 5
3,5-Dinitrobenzonitrile	95 ± 5
2,4,6-Trinitrotoluene	50 ± 5

The conclusion that these complexes are "charge-transfer" in character is supported by the finding that the increased absorption at *ca.* 650 mμ (see Figure) becomes resolvable into a distinct new band, when axial ligands such as pyridine are present in solution.

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