INFLUENCE OF STRUCTURAL FACTORS ON THE SPECTRAL AND LUMINESCENCE PROPERTIES OF METALLOPORPHYRINS*

V. A. Mashenkov, K. N. Solov'ev, and G. D. Egorova


On the basis of a study of the influence of alkyl substitution on the absorption spectra of metalloporphyrins, the nodal properties of the optical $\pi$ electrons, obtained in the MO LCAO method, have been confirmed. It has been established that alkyl substituents have a comparatively marked influence on the phosphorescence yield. In a study of the influence of additional complex formation on the phosphorescence, it has been shown that the effect of conjugation plays a significant part in removing the intercombination exclusion when heavy atoms are present in the molecule. It has been concluded that the $D_{4h}$ symmetry of the conjugated system is preserved approximately in the pyridinates of Mg porphyrins. Phosphorescence of associates of Cu porphyrins has been detected.

Metalloporphyrins, i.e., complexes of metals with various derivatives of porphine (Fig. 1), require careful study as analogs of the most important biological pigments, chlorophyll, hemoglobin, cytochromes, etc. Metalloporphyrins differ from other complexes in that on complex formation the metal atom is introduced into a ready-made cyclic group (the porphine ring) whose rigid geometry imposes definite requirements on the electronic structure of the metal atom. This characteristic feature at one time led to the hope that the study of metalloporphyrins would reveal certain universal properties of complex compounds, particularly in spectroscopic studies [1]. Subsequently, however, it was found that the influence of the metal on the spectrum of the metalloporphyrin involves perturbation of the $\pi$ electron cloud of the molecule and that the information on the electronic structure of the metal atom which can be gained from spectroscopic data is indirect [2]. This feature means that the results obtained for metalloporphyrins are specific. It is this specificity, however, which is of particular interest in connection with the important part played by metalloporphyrins in living nature. It may be noted that the part played by the magnesium atom of the chlorophyll molecule in photosynthesis is at present not completely clear. The present paper gives the results of a study of the dependence of the spectral and luminescence properties of metalloporphyrins on a number of factors: the structure of the macroring; the nature of the metal; the introduction of additional ligands; and association of the molecules.

We studied the complexes of porphyrins with the following metals: Mg$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, Pd$^{2+}$. The complexes with copper and nickel were prepared by boiling a solution of the corresponding porphyrin in absolute acetic acid with the metal acetate [3]. When the porphyrin being studied was sufficiently pure, the metal derivative obtained contained no impurities, since the reaction takes place quantitatively. The corresponding reaction with zinc had to be carried out under milder conditions; a solution of the porphyrin in methanol was heated to boiling with zinc acetate by the method described, for example, in [4]. Zn porphyrine was prepared by direct synthesis from Mannich's base (2-dimethylaminomethylpyrrole) and zinc acetate in pyridine with heating in a sealed ampul. Mg etioporphyrin was prepared by the method described in [3] using ethylmagnesium bromide. The Pd derivatives were prepared by double decomposition. The

* Presented at the Second All-Union Conference on the Use of Physical Methods in the Chemistry of Complex Compounds (Kishinev, October 1965).
porphyrin was dissolved in absolute ethanol. Metallic sodium was added to this solution until all the free base was converted into the sodium salt (the reaction was followed using a visual spectroscope). Palladium (II) chloride was also dissolved in absolute ethanol. When these two solutions were mixed, the sodium was replaced by palladium. The reaction takes place under mild conditions without heating and almost instantaneously.

Fig. 2. Absorption spectra of metalloporphyrins in benzene. 1) Cu octaethylporphine; 2) Cu α,β,γ,σ-tetrapropylporphine; 3) Zn α,β,γ,σ-tetrapropylporphine; 4) Ni α,β,γ,σ-tetrapropylporphine; 5) Pd α,β,γ,σ-tetrapropylporphine.

The methods used to prepare the porphyrins used as ligands are described below. Porphine was prepared from Zn porphine by decomposition with HCl and as a side product of the synthesis of chlorine. Chlorine (dihydroporphine) was prepared by the method described by Eisner and Linstead [5] from Mannich's base and ethylmagnesium bromide, with subsequent purification on magnesium oxide. a,β,γ,σ-Tetrapropylporphine was prepared in fairly good yield by condensing butyraldehyde with pyrrole in the presence of zinc acetate (a modification of Rothemund's reaction [6]). The reaction was carried out over a period of 24 hr at a temperature of 150°C. The product was purified by ether-acid distribution and chromatography on alumina and magnesium oxide. Octaethylporphine was prepared by condensing S-bromo-3, 4-diethylpyrryl-5-methyl-3, 4-diethylpyrrolylpyrrolenylmethene (perbromide) in succinic acid [7]. The final purification was carried out on alumina with a chloroform-petroleum ether mixture (1:3). Etioporphyrin I (1,3,5,7-tetramethyl-2,4,6,8-tetraethylporphine) was prepared by heating brominated cryptopyrromethene hydrobromide with formic acid [3] with subsequent purification on alumina. N-Methyloctaethylporphine and N-methyletioporphyrin were synthesized from the corresponding porphyrins and methyl iodide by heating in an ampul at 100°C [4].

The metalloporphyrin molecules have highly symmetrical conjugated systems (exact or approximate D₄ᵥ symmetry depending on the edge substituents present). The absorption spectra of the metalloporphyrins generally consist of two weak bands in the visible range, one of which is of vibrational origin (first electronic transition) and a Soret band at about 400 nm (second electronic transition) [2]. The fluorescence spectra of the metalloporphyrins are approximately mirror-symmetrical with respect to the two long-wave absorption bands. The phosphorescence spectra, observed in frozen solutions at low temperatures, have a vibrational structure analogous to the vibrational structure of the low-temperature fluorescence spectra, and are distinguished by the high intensity of the first band (O–O transition). The luminescence yield depends to a marked extent on the nature of the metal; the Mg derivatives are characterized by strong fluorescence and weak phosphorescence, for the zinc complexes both forms of luminescence are commensurate, for the complexes with copper and palladium only fluorescence is characteristic, and the Ni derivatives do not exhibit luminescence.† The influence of the nature of the metal on the absorption spectrum is slight and is reflected in the position of the spectral bands and the ratio of their intensities, high stability of the complexes corresponding to displacement of band I towards shorter wavelengths. The preservation of the general character of the spectrum with change in the nature of the metal indicates that for the optical electrons the interaction with the metal can be treated as a comparatively slight

† Contrary to the results given in [8–10], we did not detect luminescence of the Ni porphyrins with increase in the sensitivity by three orders of magnitude relative to the Cu porphyrins.