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PORPHYRINS

VI.* ABSORPTION SPECTRA AND ASSOCIATION OF METAL COMPLEXES OF meso-FORMYLETIOPORPHYRIN

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UDC 543.422.4.6 : 547.749 : 541.49

A magnesium complex of meso-formyletioporphyrin I (FEP) was obtained by reaction of FEP with methylmagnesium iodide. The electronic and IR spectra of FEP and its complexes with copper, zinc, nickel, cobalt, and magnesium in solutions and crystalline films were investigated. It is shown that the changes in the electronic spectra as the temperature of the solutions is lowered are due to association of the molecules of the metal complexes (M–FEP) of the metal–formyl type. Association of the molecules in solid films is accomplished through $\pi-\pi$ electron interaction of the porphyrin rings. The Mg–FEP complex, the molecules of which associate through a metal–formyl interaction both in solution and in films, constitutes an exception to this.

meso-Formylporphyrins have weaker reactivities with respect to the carbonyl group than the sterically unhindered β-formylporphyrins or aromatic aldehydes. For example, the formation of Schiff bases, oximes, hydrazones, and other carbonyl-group derivatives proceeds only at high temperatures [2-5].

During a study of the reaction of meso-formyletioporphyrin I (FEP) with a Grignard reagent in ether we observed that the reaction product has an unusual electronic spectrum in which the α and β bands in the visible region of the spectrum that are characteristic for metal complexes were practically absent and an intense broad band at 650-670 nm was present. Treatment of this substance with trifluoroacetic acid gave FEP, and this unambiguously indicated retention of the meso-formyl group in the reaction of porphyrin with methylmagnesium iodide and the formation of only Mg–FEP as a result of the reaction. Attempts to obtain Mg–FEP in the crystalline state were unsuccessful, since a polymeric dark-green film, which sub-

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* For communication V, see [1].

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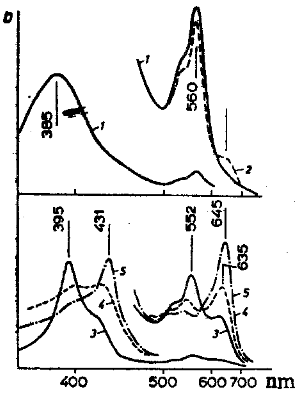


Fig. 1

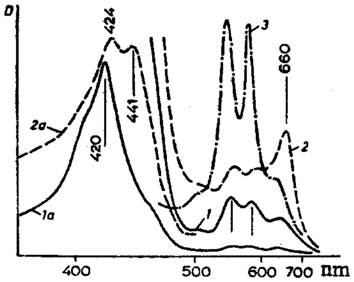


Fig. 2

Fig. 1. Absorption spectra of Co–FEP in various states: 1) sublimate on a plate at 20°C; 2) sublimate on a plate cooled to −196°; 3), 4), and 5) solution in methylene chloride–trichloroethylene at +20, −90, and −196°.

Fig. 2. Absorption spectra of solutions of Zn–FEP: 1) and 1a) in methylene chloride–trichloroethylene; 2) and 2a) the same solutions after cooling to −196°C; 3) in THF–ether (1 : 1) at −196°.

sequently dissolved only after prolonged refluxing in a large amount of solvent, was formed in a concentrated solution of the complex in ether or chloroform. The addition of solutions of metal acetates in methanol to a green solution of Mg–FEP in chloroform led to displacement of the magnesium ion from the porphyrin molecule by another ion to give a more stable metal complex, which precipitated from the solution in the form of large bright-red crystals via the scheme

$$\text{Mg-FEP} + \text{M(OAc)}_2 \longrightarrow \text{M-FEP} + \text{Mg(OAc)}_2,$$

where

$$\text{M} = \text{Cu}^{+2},\ \text{Zn}^{+2},\ \text{Ni}^{+2},\ \text{Co}^{+2}.$$

We observed that a characteristic feature of the electronic spectra of all of these compounds is the presence of a band at 650 nm, the intensity of which depends on the nature of the central metal atom, the concentration of the substance, and the solvating properties of the solvent [6]. Any modification of the formyl group must lead to disappearance of the band at 650 nm. For example, the long-wave band is absent in the electronic spectra of meso-acetylporphyrins, in which the carbonyl group is completely removed from conjugation with the π system of the ring because of the considerable steric effects of the adjacent alkyl substituents, whereas the general form of the electronic spectrum differs only slightly from the spectra of octaalkylporphyrins [7].

In order to ascertain the structure and character of the association of the FEP and M–FEP molecules we investigated the electronic and IR absorption spectra of these compounds in solutions at various temperatures and in the solid state.

Electronic Spectra

We investigated the dependence of the intensity of the absorption band of M–FEP at 650 nm on the temperature. The electronic spectra of various M–FEP at various temperatures in methylene chloride–trichloroethylene are presented in Figs. 1-4. A decrease in the temperature of the solutions leads to the same spectral changes as those observed when the concentration is increased [6]. Hence it may be concluded that there is a similarity in the nature of the molecular association that is manifested at low concentrations or at low temperatures.

Like concentration association, the low-temperature association of M–FEP depends on the central metal atom. Association is manifested most graphically in the spectra of Mg–FEP (Fig. 4). Under the same conditions the spectra of Cu–FEP change only slightly as the temperature is lowered. Zinc–, nickel–, and cobalt–FEP occupy an intermediate position with respect to their tendency to undergo association (Figs. 1-3). In solutions containing ether, which may form a bond with the metalloporphyrin, Zn–FEP associates considerably more weakly than in methylene chloride–trichloroethylene.

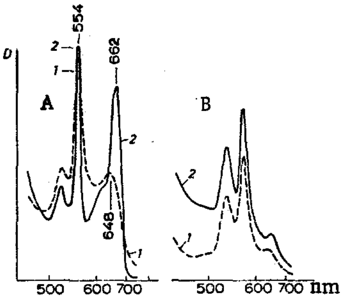


Fig. 3

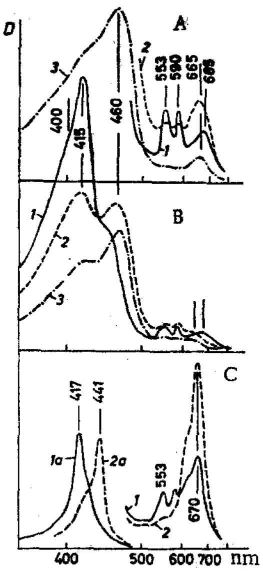


Fig. 4

Fig. 3. Absorption spectra of solutions of Ni–FEP (A) and Cu–FEP (B) in methylene chloride–trichloroethylene at 20°C (1) and −196° (2).

Fig. 4. Absorption spectra of Mg–FEP in various states: A) and B) sublimates of various thicknesses (on plates at 20°C): 1) starting layers; 2) after heating for a few minutes at 250°; 3) after heating at 260-270° (the thickness of the layers decreased as a result of incipient sublimation); C) solutions in methylene chloride–trichloroethylene at 20° (1, 1a) and −196° (2, 2a).

It seemed logical to extend the study of the concentration dependence of the spectra of M–FEP to the limiting case, i.e., to the solid state. We were able to obtain the spectra of sublimed films of the substances, since FEP and M–FEP sublime satisfactorily without appreciable decomposition in vacuo at and above 270°. In control experiments in which the sublimates were dissolved they behaved like the unsublimed products.

In contrast to solutions [6], the character of the associates in sublimed layers is independent of the metal atom in the case of Cu–, Ni–, and Zn–FEP. In the case of sublimation on a support at 20° the Co–FEP molecules preferentially orient themselves in such a way that the interactions responsible for the appearance of the long-wave band do not develop. Heating the Co–FEP layer until it had sublimed completely did not lead to appreciable spectral changes. Only the $\pi-\pi$ interaction between the tetrapyrrole rings of adjacent molecules, which shows up only as a certain slight broadening of the bands, evidently predominates under these conditions. The appearance of a long-wave band in the spectrum of a sublimed layer of Co–FEP can be stimulated to a certain extent if sublimation is carried out on a cooled support on which an ordered orientation of the molecules is less likely, and, as a result of their relatively chaotic orientation, some of the molecules are favorably oriented for a metal–formyl interaction. Relatively weak absorption at ~650 nm is therefore observed at −196° in the spectrum of a sublimed film of Co–FEP (Fig. 1). This absorption decreases somewhat when the sample is heated to 20°, but it does not disappear completely.

Like the spectra of Co–FEP, the electronic spectra of sublimed films of Zn–FEP, Ni–FEP, and Cu–FEP obtained by sublimation on plates at 20° did not contain signs of association of the formyl–metal type: their spectra contain unshifted solitary Soret bands and α and β bands at 500-600 nm, and the long-wave band is absent. The maxima in the spectrum of Zn–FEP are found at 388, 528, and 558 nm, as compared with 393, 533, and 566 nm for Ni–FEP and 390, 545, and 580 nm for Cu–FEP.

The spectrum of a sublimed film of Mg–FEP differs substantially from the spectra of films of the other FEP complexes (Fig. 4). In addition to the α and β bands, it contains an absorption band at 685 nm, and the Soret band is shifted to the long-wave region and consists of at least three components: the most intense com-

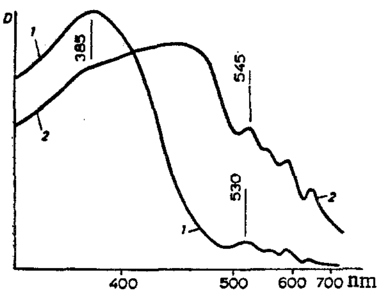


Fig. 5

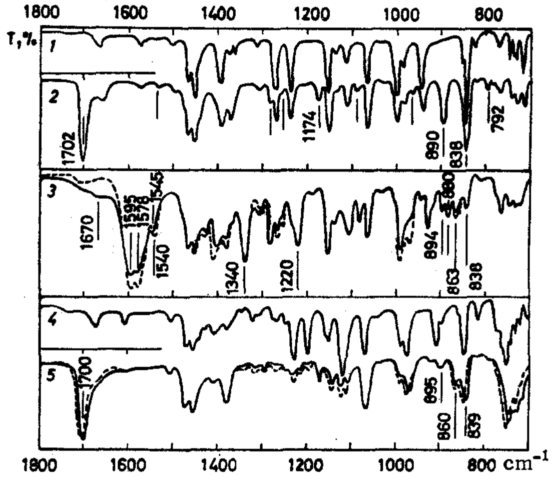


Fig. 6

Fig. 5. Absorption spectra of a sublimed film of FEP prior to (1) and after (2) heating at a temperature close to the sublimation temperature.

Fig. 6. IR spectra of sublimed films: 1) Ni–EP; 2) Ni–FEP; 3) Mg–FEP prior to (continuous line) and after (dash line) heating at 255-260°C for 10 min; 4) EP; 5) FEP prior to (continuous line) and after (dash line) heating at 180-190° for 20 min.

ponent at 415 nm and shoulders at 460 and 400 nm. It may therefore be assumed that a large portion of the Mg–FEP molecules in the sublimed layer are associated by an interaction of the formyl–metal type in which there may be two forms of associates of this type: the maximum of the Soret band at 415 nm corresponds to one of them, and the shoulder at 460 nm corresponds to the other. The shoulder at 400 nm evidently corresponds to molecules associated via a $\pi-\pi$ interaction.

The Mg–FEP associates with a Soret band at 415 nm are converted to associates of another form with a Soret band at 460 nm (Fig. 4) when the sublimed layer is heated near the sublimation temperature (above 250°). During this transformation the intensities of the α and β bands decrease, and the long-wave band increases and its maximum is shifted from 685 to 665 nm. On the whole, the spectral changes observed when the sublimed layer of Mg–FEP is heated resemble the spectral changes observed when a solution of the complex is cooled.

When comparing the spectra of solutions and films of etioporphyrin (EP) and FEP one should note that the character of the spectrum of EP depends relatively little on the aggregate state, while the spectra of films and solutions of FEP differ substantially. Broadening of the Soret band and its shift to the short-wave region from 408 to 385 nm are characteristic for the spectrum of a film of FEP at 20°. There is an appreciable change in the spectrum of a film of FEP when it is heated: the Soret band is shifted markedly to the long-wave region, there is an overall increase in the absorption in the visible region, and the bands at 500-700 nm undergo relatively small shifts.

Infrared Spectra

From a comparison of the IR spectra of sublimed films of Ni–FEP and Ni–EP it is apparent that the spectrum of Ni–FEP is practically a simple superimposition of the spectrum of unsubstituted Ni–EP and several additional bands, which can evidently be assigned to the formyl group (Fig. 6). Specifically, these (indicated by arrows on curve 2 of Fig. 6) include the ν_{CO} band at 1702 cm^{-1}, the δ_{CH} band at 890 cm^{-1}, and the band at 1174 cm^{-1}. The Zn–FEP, Co–FEP, and Cu–FEP complexes have similar characteristics in their IR spectra.

The absence of an appreciable effect of a formyl group on the frequencies of the vibrations of the tetrapyrrole skeleton of M–FEP constitutes evidence for the complete absence of conjugation between them when the substance exists in the crystalline state in the form of a sublimed film. This fact confirms our earlier assumption that the formyl group is found outside of the plane of FEP [2].

The spectrum of the Mg–FEP sublimate has a completely different structure. There are up to five overlapped absorption bands in the 1500-1700 cm^{-1} region in which the ν_{CO} vibrations are found (Fig. 6). The

TABLE 1. Characteristics of the Compounds Obtained

Compound	Found, %			Empirical formula	Calculated, %		
	C	H	N		C	H	N
Zn-FEP	69,6	6,1	9,9	$C_{33}H_{36}N_4OZn$	69,5	6,4	9,8
Ni-FEP	70,25	6,2	9,6	$C_{33}H_{36}N_4ONi$	70,4	6,4	9,9
Co-FEP	70,3	6,2	9,7	$C_{33}H_{36}N_4OCo$	70,4	6,4	9,9
Mg-FEP	74,2	7,2	10,2	$C_{33}H_{36}N_4OMg$	74,9	6,9	10,6

δ_{CH} band of the formyl group is split into two components (880 and 894 cm^{-1}). In addition, completely new bands at 1340 and 1220 cm^{-1}, which are not observed in the spectra of the other M–FEP and M–EP, are observed, and the δ_{CH} band of the methylidyne groups is evidently split into two bands (838 and 863 cm^{-1}). The corresponding band in the spectra of Ni–EP and Ni–FEP is found at 838 cm^{-1}. All of these peculiarities can hardly be explained only by a molecular association of the $\pi-\pi$ interaction type. They constitute evidence for the strong mutual influence of the formyl group and the tetrapyrrole skeleton, which can evidently enter into conjugation under the given conditions. The splitting of the δ_{CH} bands of the methylidyne groups, the decrease in the ν_{CO} frequency, the appearance of new bands in the IR spectrum, and the shift of the bands in the electronic spectrum may also be a consequence of this conjugation. The splitting of the ν_{CO} band into several components may be due to the different forms of intermolecular and intramolecular interactions of the formyl group.

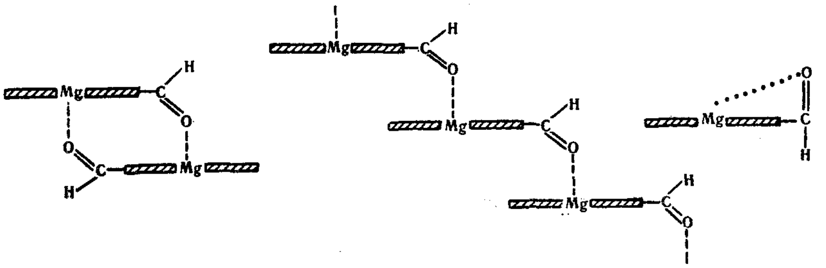
By comparing the spectra of FEP and EP one can see that the spectrum of FEP cannot be the simple sum of the absorption frequencies of EP and the formyl group. It is difficult to compare the bands of FEP and EP. The δ_{CH} band of the methylidyne protons is split into two components (839 and 860 cm^{-1}) in both the spectrum of the Mg–FEP sublimate and the spectrum of FEP. The ν_{NH} band of the imino groups in the spectrum of EP is found at 3325 cm^{-1} and has a half-width of ~25 cm^{-1}, whereas the ν_{NH} band in the spectrum of FEP is shifted to 3295 cm^{-1} and its peak intensity is reduced, but the half-width is increased to 50 cm^{-1}. The broadening and the somewhat asymmetrical ν_{NH} contour in the spectrum of FEP make it possible to assume splitting of this band into two components. Despite such a substantial difference between the IR spectra of FEP and EP, one can hardly assume the possibility of conjugation between the formyl group and the porphyrin ring, since the ν_{CO} band is found at 1700 cm^{-1}, which is characteristic for the unconjugated formyl group. The reasons for the spectral peculiarities of FEP evidently lie in the peculiarities of its molecular symmetry, conformation, and molecular association in the sublimed layers.

Heating sublimed layers of FEP and Mg–FEP up to the sublimation temperatures of the compounds, which leads to such significant changes in their electronic spectra, does not give rise to any appreciable changes in the IR spectra (Fig. 6). The ν_{CO} frequency is increased to a small extent (5 cm^{-1}) in the spectrum of FEP, and there is therefore no basis to assume the possibility of participation of the formyl groups in associations. The $\pi-\pi$ interactions evidently play the deciding role in association at high temperatures. The certain increase in the δ_{CH} frequencies of the methylidyne bridges (839 and 860 cm^{-1}) when the FEP layer is heated confirms this conclusion.

When the Mg–FEP layer is heated, one of the components (at 1670 cm^{-1}, the component with the weakest intensity) of the complex ν_{CO} band vanishes in its IR spectrum, and the remaining components are intensified somewhat. On the whole, however, the IR spectrum does not change much (Fig. 6). It might be supposed that the changes in the electronic spectrum that accompany heating are due, as in the case of FEP, to a change in the $\pi-\pi$ interaction in the layer. Any change in the interaction between the porphyrin rings with participation of the formyl group should have led to substantial changes in the ν_{CO} band, but this does not occur either in the spectrum of FEP or in the spectrum of Mg–FEP.

In summing up the results of the study of the electronic and IR spectra of FEP and M–FEP one may express an assumption regarding the nature of the molecular association of these compounds. Since only Mg–FEP had electronic and IR spectra that differ sharply from those of the remaining metal complexes, the formation of different associates of the magnesium–formyl type, the schematic structure of which is presented below, is characteristic for it both in sublimed films and in solution.

The other metal complexes are solvated in dilute solutions in chloroform or methylene chloride–trichloroethylene and exist primarily in the form of monomers. A decrease in the temperature sharply increases the ability of the compounds to undergo association; this is manifested as an increase in the intensity of the band at 650 nm in the spectra of a number of metal complexes. Thus the band at 650 nm may serve



as a characteristic of an interaction of the metal–formyl type. On the other hand, the presence of weak but sufficiently distinct bands at 650 nm in the spectra of solutions of FEP and Cu–FEP at various dilutions indicates the fact of a weak but appreciable interaction of the formyl group with the π system of the porphyrin ring. This interaction is evidently possible only under the condition of distortion of the planar structure of the porphyrin and the creation of this conformation of the molecule as a whole when there is a possibility of some conjugation of the formyl group with the porphyrin ring. The absence of a band at 650 nm in the spectra of films of both free FEP and its Cu, Zn, Ni, and Co complexes indicates, first, that in the crystalline state the conformation of the molecules does not ensure interactions of the formyl group with the porphyrin ring and, second, that the mutual orientation of the molecules is due only to a π–π interaction vis-a-vis complete absence of an interaction of the metal–formyl type. However, as recently demonstrated [8] in the case of the Zn complex of meso-formyloctaethylporphyrin, disruption of the crystallinity of the metal complex leads to pronounced changes in the IR spectrum; this is evidently associated with the possibility of intermolecular interaction of the metal–formyl type and, as a consequence of this interaction, with the change in the conformation of the complex.

EXPERIMENTAL

The complexes of FEP with Cu, Co, Zn, and Ni were prepared by the standard method, which consisted in refluxing a solution of 100 mg of FEP and 200 mg of the appropriate metal acetate in a mixture of 50 ml of chloroform, 10 ml of acetic acid, and 10 ml of methanol for 10-15 min. At the end of the reaction (as determined by spectrophotometric monitoring), the reaction mixture was vacuum evaporated, and the residue was washed with hot water and methanol. It was then chromatographed on silica gel, and the chromatographic product was crystallized from chloroform–methanol (10:1) to give the metal complexes in practically quantitative yields. The Mg–FEP complex was obtained by refluxing a solution of 100 mg of FEP in 50 ml of ether in the presence of methylmagnesium iodide (obtained from 100 mg of magnesium) for 1 h. At the end of the reaction, the solution was treated with water, and the organic layer was separated and dried. The reaction products were then chromatographed on activity II aluminum oxide to give Mg–FEP in 50-60% yield. The results of elementary analysis are presented in Table 1. Solid layers of FEP and M–FEP were obtained by vacuum sublimation on quartz plates or on KBr plates. The spectra of solutions of M–FEP in methylene chloride–trichloroethylene (1:2) were recorded. Drying of the solvents and all of the manipulations with the solutions, including the spectral measurements, were carried out under vacuum conditions in 1-mm thick cuvettes. The electronic spectra were obtained with a Shimadzu SV-50 spectrophotometer. The IR spectra were recorded with a Perkin–Elmer 457 spectrometer.

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