Self-assembly of *meso*-mono-4-pyridyltriphenylporphyrinatoiron(II) in sublimed layers. Interaction with molecular oxygen

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Low-temperature (T = 80 K) interaction of the sublimed layers of *meso*-mono-4-pyridyltriphenylporphyrinatoiron(II) (FeMPyTPP) with dioxygen was studied by IR and electronic absorption spectroscopies. Unlike the *meso*-tetraphenylporphyrinatoiron(II) (FeTPP) layers, coordination of O_2 with FeMPyTPP produces extra-complexes of two types: in the first complex one of the axial sites is free, while in the second complex an axial site is occupied by the pyridine group of the adjacent molecule. The results obtained indicate self-assembly of the FeMPyTPP molecules through coordination bonds between the iron atom and pyridine group of the adjacent molecule in the layer. The bonding of O_2 by the sublimed FeMPyTPP layers differs substantially from that by the FeTPP layers, which rapidly loose their ability of oxygen bonding at room temperature.

Key words: *meso*-mono-4-pyridyltriphenylporphyrinatoiron(II), sublimed layers, oxygen mediators, electronic absorption spectroscopy, IR spectroscopy.

Reversible bonding of dioxygen is one of the most important properties of *heme*-containing and related compounds, providing them biological and catalytic activity.[1,2] Some metal porphyrins, being efficient oxygen mediators, are of interest as oxygen absorbers,[3] artificial hemoglobin,[4] and membranes with selective oxygen permeability.[5]

Thin porphyrin layers are promising for the use in photovoltaic cells,[6] gas sensors,[7] and heterogeneous catalytic systems.[8,9]

Studies of sublimed layers of *meso*-tetraphenylporphyrinatoiron(II) (FeTPP)[10] and structurally similar *meso*-tetra-4-pyridylporphyrinatoiron(II) (FeTPyP)[11] have shown that these films loose their O_2-bonding ability after storage at room temperature. In the FeTPyP layers this process is strongly retarded, and the spectral data indicate that this is caused by the formation hexacoordinate saturated complexes in the layer due to the interaction of the metal ions with the pyridine groups of the adjacent molecules. It could be expected that a decrease in the number of pyridine groups in the *meso*-positions of the porphyrin macrocycle (to the ratio of the number of metal ions to pyridine groups equal to unity) would diminish the probability of formation of hexacoordinate structures and improve the oxygen-bonding characteristics of the layer.

In this work, we synthesized *meso*-mono-4-pyridyltriphenylporphyrinatoiron(II) (FeMPyTPP) and studied the O_2-bonding ability of its sublimed layers prepared under various conditions.

Experimental

Monopyridyltriphenylporphyrin (H_2MPyTPP) was synthesized using the method of mixed aldehydes.[12] Its purity was confirmed by the data of thin-layer chromatography, NMR, and UV spectroscopy coincided with the published data.[12] Since the Fe^{II} porphyrin complexes are readily oxidized in air to form μ-oxo dimers, we used stable in air hexacoordinate dipiperidine extra-complex FeMPyTPP(Pip_2) (Pip is piperidine) synthesized from H_2MPyTPP using a described procedure.[13]

A weighted sample (~10 mg) of FeMPyTPP(Pip_2) was placed in a Knudsen cell and stored in high vacuum (~10^{-5} Torr) at ~250 °C for ~3 h. This storage results in the elimination of the axial ligands (monitored by measurement of the pressure at the outlet of the cryostat). Then at the same pressure the temperature of the cell was raised to 300—320 °C, and FeMPyTPP was sublimed at this temperature. To prepare layers with a thickness convenient for IR spectroscopic measurements, sublimation was carried out for 2—3 h, while it took several of minutes to record electronic absorption spectra (EAS) at the Soret band or several tens of minutes for recording bands in the visible region. The CsI and CaF_2 plates (for recording IR spectra and EAS, respectively) placed inside an optical cryostat were cooled with liquid

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nitrogen and used as supports. Thoroughly dried above P_2O_5 and precooled oxygen was slowly supplied to the cryostat from a receiver equipped with a manometer, which measured the equilibrium pressure in the cryostat. Further the sublimed layer was stored for ~30 min, and the temperature was changed in the following sequence: 80 → 120 → 80 K. Then oxygen was removed, and EAS or IR spectra were recorded.

IR spectra were recorded on a Specord M-80 spectrophotometer. The spectral gap width was 4 cm^{-1}. Electronic absorption spectra were obtained on a Specord M-40 spectrophotometer. NMR spectra were recorded using a Varian Mercury 300 spectrometer in a $CDCl_3$ solution.

Results and Discussion

When O_2 is let on the thin (to 5 μm) FeMPyTPP layers prepared by sublimation on a surface cooled by liquid nitrogen, two new bands at 1150—1200 cm^{-1} (see Fig. 1, *b*) appear in the IR spectrum. They are localized in the immediate vicinity of the absorption band of the metal porphyrin at 1178 cm^{-1} (Fig. 1, *a*) and can distinctly be seen only in the difference spectra (Fig. 1, *c*) with maxima at 1184 and 1173 cm^{-1}. An increase in the temperature of the layer to 200 K followed by cooling results in an increase in the intensity of the low-frequency band (Fig. 1, *d*). When oxygen is let on the layer prepared by sublimation of the porphyrin on the surface at room temperature, mainly the low-frequency band with a maximum at 1173 cm^{-1} appears in the difference spectrum.

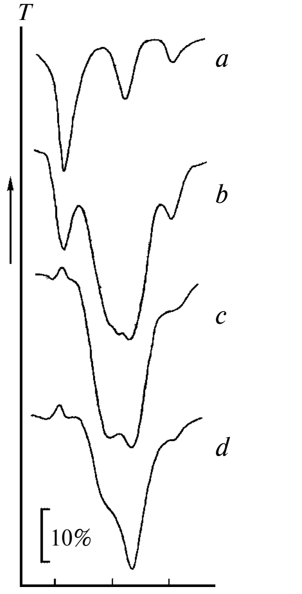

Fig. 1. IR spectrum of the sublimed FeMPyTPP layer at 80 K in the $\nu(O_2)$ region of coordinated dioxygen (*a*), after inlet of O_2 (28 mm Hg) into a cryostat and annealing in the 80 → 120 → 80 K cycle (*b*), difference spectrum *b—a* (*c*), and difference spectrum after the 80 → 200 → 80 K cycle (*d*).

Two absorption bands of stretching vibrations of the coordinated O_2 and a change in their intensity after temperature training of the sample are similar to those observed previously for the sublimed CoMPyTPP samples.[14] However, for the latter the difference in the $\nu(O_2)$ frequencies of two new bands is 80 cm^{-1}, and the presence of two types of bound O_2 is manifested in the IR spectra to a greater extent.

The EAS (Fig. 2) undergo remarkable changes in the presence of O_2 also upon temperature training of the sample. The Soret band in the low-temperature sublimed FeMPyTPP sample exhibits a long-wave shoulder at 435 nm. In the presence of O_2, the maximum of the band undergoes a bathochromic shift (dotted line), which increases after sample training in the 80 → 200 → 80 K cycle (see Fig. 2, dotted line). The band in the visible region behaves similarly. For the sample heated to room temperature under dynamic vacuum (see Fig. 2, dotted line) where the oxygen complex decomposes, the maximum of the Soret band shifts toward the wavelength region in which the long-wave shoulder was earlier observed. The band in the visible region structurizes and manifests a pronounced shoulder at 600 nm. An analogous EAS is observed for the sublimed samples prepared by deposition on the surface at room temperature. Unlike the IR spectra, manifestations of dioxygen coordination in the EAS of FeMPyTPP are much stronger than those for the previously studied[14] CoMPyTPP complexes.

These results can be interpreted as follows. The absorption of O_2 by the low-temperature sublimed FeTPP samples with microporosity and ability to coordinate potential ligands over the whole layer thickness has previously[10] been found. The band at 1187 cm^{-1} was assigned[10] to $\nu(O_2)$ in the pentacoordinate $O_2 \cdot$FeTPP adduct found previously[15] in an argon matrix with $\nu(O_2)$ = 1195 cm^{-1}. In similar experiments[11] with *meso*-tetra-4-pyridylpor-

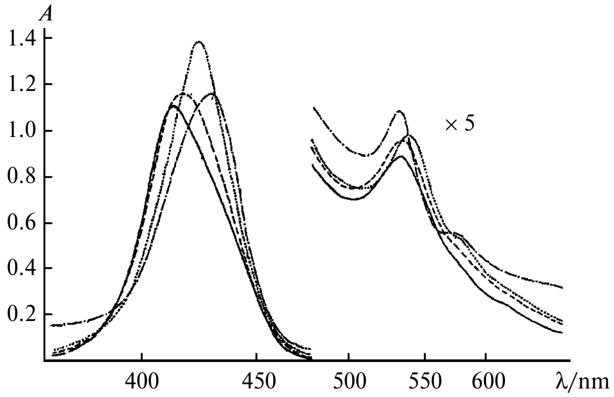

Fig. 2. Electronic absorption spectrum of the sublimed FeMPyTPP layer at 80 K before (solid line) and after inlet of O_2 (30 mmHg) into a cryostat and annealing in the 80 → 120 → 80 K (dotted line) and 80 → 200 → 80 K (dashed line) cycles, and after heating of the layer *in vacuo* to room temperature (dashed line).

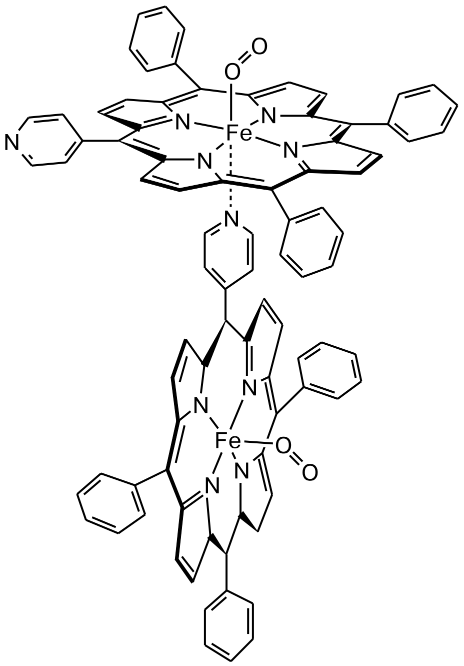

Fig. 3. Structures of the penta- and hexacoordinate dioxygen complexes in the sublimed FeMPyTPP layer.

phyrinatoiron(II), the ν(O_2) band appeared at 1172 cm^{-1} and was attributed to a hexacoordinate complex, whose fifth coordinate is occupied by the pyridine group of the adjacent molecule in the layer. Thus, it seems reasonable to assign the new bands found in our work for FeMPyTPP to two types of dioxygen complexes schematically shown in Fig. 3. Indeed, when additional electron-donating ligands, such as nitrogen-containing bases, are coordinated to the sixth coordinate, ν(O_2) decreases and ν(M—O_2) increases compared to those of the pentacoordinate complexes.[2] This is related to the additional transfer of the electron density through the *d*-orbitals of the metal to the antibonding π^*_g-orbitals of the oxygen atom, strengthening the M—O_2 bond and weakening the O—O bond. For example, for the pentacoordinate FeTPP(O_2) complex prepared in the argon matrix, the ν(O_2) band is at 1195 cm^{-1}, while it is observed at 1157 cm^{-1} in the spectrum of the hexacoordinate (Pip)FeTPP(O_2) complex.[16] We found no IR data on ν(O_2) of the PyFeTPP(O_2) complex. However, in the spectrum of the PyFe(Cap)O_2 complex, where Fe(Cap) is the "capped" porphyrin,[17] ν(O_2) is 1175 cm^{-1},[18] which is very close to that observed by us. The influence of the electron-donating ligand in the sixth coordinate on ν(O_2) of the coordinated dioxygen is much stronger in the cobalt porphyrins[14] than in the iron porphyrins, which is commonly explained by the multiplet character of the M—O_2 bond in the latter.[19]

The EAS of the low-temperature FeMPyTPP layer heated *in vacuo* or the layer prepared by sublimation on the surface at room temperature is close to the spectra of solutions of *meso*-substituted ferroporphyrins in the pentacoordinate high-spin state.[20—22] Such a pattern is observed when a nitrogen base acts as an extra-ligand. At the same time, the dioxygen complex exists in the low-spin state,[22] whereas the ferroporphyrin containing no axial ligands demonstrates the state with an intermediate spin.[23] Since the energies of the d_π-orbitals of iron and e_g-orbitals of porphyrin are close, the EAS are very sensitive to the spin state of Fe atom in the complex. This is clearly confirmed by the spectra presented in Fig. 2.

The amounts of bound oxygen in the sublimed FeTPP layers stored *in vacuo* at room temperature followed by cooling and oxygen supply are insufficient for its spectroscopic detection. The FeTPP layers prepared by sublimation on the surface at room temperature behave similarly. At the same time, in both the first and second cases, the FeMPyTPP layers remain active toward O_2 binding. These layers retain their activity for much longer time (for weeks) than the FeTPyP layers, which loose completely their ability to coordinate O_2 for a week. The spectroscopic measurements show that the FeMPyTPP layers, unlike FeTPP, are oxidized very slowly (increase in the ν_{as}(Fe—O—Fe) band of the μ-oxo dimer at 870 cm^{-1}) even upon storage in air.

These differences in the oxygen-bonding ability of the sublimed layers of the structurally similar compounds can be attributed, in our opinion, to their supramolecular structure. In the *meso*-tetraarylporphyrin compounds, whose aryl groups contain no functional substituents capable of specific intermolecular interactions, the molecules are arranged in layers with parallel planes of the porphyrin cycles.[24] When such interactions occur (hydrogen bonds, coordination, *etc.*), the supramolecular organization of the system can substantially change.[25—28]

In the 4-pyridyl-substituted derivatives, the intermolecular coordination compels adjacent molecules to be arranged perpendicularly to each other. The freshly sublimed FeMPyTPP layers consist of structures containing both above types of supramolecular organization. Such a system is thermodynamically nonequilibrium and can be transformed in time into a more stable system with prevailing of the pentacoordinate FeMPyTPP molecules. Since the phenyl groups predominate in the *meso*-positions, the probability of formation of the hexacoordinate saturated structures is low. The mutually perpendicular arrangement of the adjacent molecules favors the layer to retain porosity[28] and ability to link various ligands. It is likely that this structure also prevents, to a great extent, μ-oxodimerization, which proceeds through the formation of complexes with the bridging dioxygen molecule. Such compounds were detected in solutions at low temperatures by NMR [29] and Raman spectroscopy.[30]

Analogous conclusions about the structure of the sublimed FeMPyTPP layers have been made from the data on their interaction with CO [31] and NO.[32]

Attention of researchers[33] is presently focused on complexes of *meso*-pyridyl-substituted porphyrins because of their ability to self-assembly due to coordination of the pyridine ligand of one molecule with the metal ion of the adjacent molecule. Various supramolecular ensembles were prepared from Zn, Ru, and Os metal porphyrins. Similar properties of the Fe and Co porphyrinates, which are true biomimetics, remain virtually unstudied.

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