A spectral study of the interaction of dioxygen with sublimed layers of manganese(II) *meso*-tetraphenylporphyrinate

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The low-temperature interaction of sublimed layers of manganese(II) *meso*-tetraphenylporphyrinate (MnTPP) with O_2, which has previously been observed only in solutions and in an inert gas matrix, was found by electron absorption and IR spectroscopy. The coordination of O_2 with sublimed MnTPP layers is only partially reversible. Bands that can serve as IR-spectral markers characteristic of the high-spin Mn^{II} ion in MnTPP and its axial complexes were observed.

Key words: manganese(II) *meso*-tetraphenylporphyrinate, sublimed layers, dioxygen coordination, electron absorption spectroscopy, IR spectroscopy.

Reversible coordination of molecular oxygen with metalloporphyrins plays an important role in biological[1] and catalytic processes.[2,3] Previously,[4–6] the capability of O_2 binding with manganese(II) *meso*-tetraphenylporphyrinate (MnTPP) molecules has been shown in the isolated state at low temperature and in an inert matrix. However, molecules in the associated state, in particular, their sublimed layers, exhibit activity in heterogeneous catalysis and electrocatalysis.

It is known[7,8] that, under specific conditions, the sublimed CoTPP and FeTPP layers are capable of reversible O_2 coordination over the whole thickness of the layer. This is due to the microporous structure of their layers, also inherent in bulky samples, which made it possible to name them "porphyrin sponges."[9] In this case, the spectral data indicate the formation of superoxide $M^{III}TPP \cdot O_2^-$ complexes. This work is devoted to electron and IR spectroscopic studies of the capability of the sublimed MnTPP layers to coordinate molecular oxygen.

Results and Discussion

The IR spectra of MnTPP in the 800—1400 cm^{-1} region before and after O_2 supply (20 Torr) on the sublimed layer are presented in Fig. 1. The band at 978 cm^{-1} that appeared in the spectrum disappears with heating the sample, indicating the formation of a thermally unstable MnTPP complex with dioxygen. This is also indicated by the electronic absorption spectra (Fig. 2). Similarly to the previously observed phenomena,[4] O_2 coordination is accompanied by considerable shifts and a decrease in the intensity of bands in the visible spectral region. A new weak band with a maximum at 830 nm appears in the near-IR region.

The frequency of stretching vibrations of the O—O bond in the IR spectrum ($\nu(O_2)$) is close to that

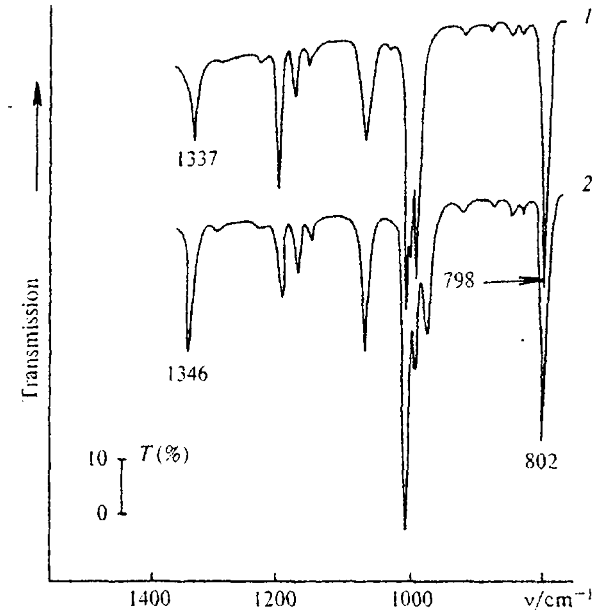

Fig. 1. IR spectra of the sublimed MnTPP layer at 80 K before (*1*) and after (*2*) O_2 supply to the cryostat at the equilibrium pressure of 20 Torr.

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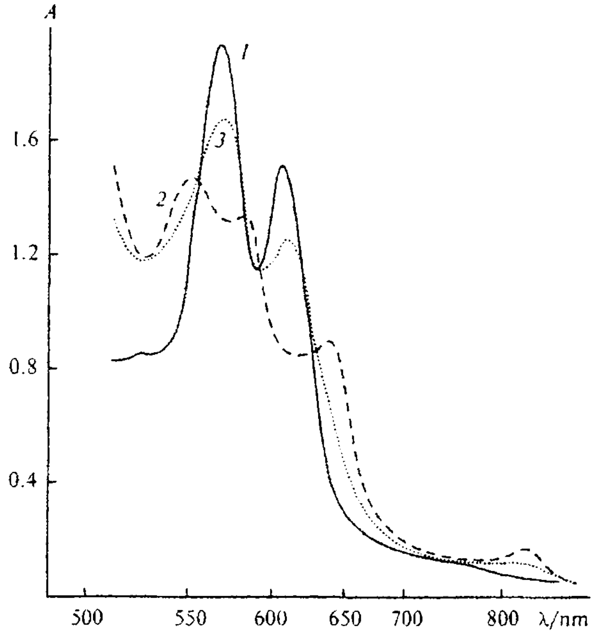

Fig. 2. Absorption spectra of the sublimed MnTPP layer at 80 K before (*1*) and after O_2 supply (20 Torr) to the cryostat (*2*) and its evacuation at 200 K for 30 min (*3*).

(983 cm^{-1})[6] of the O_2 coordinated in MnTPP · O_2 obtained in the argon matrix. In the last case, the assignment of this band to the coordinated O_2 molecules was additionally confirmed by experiments with $^{18}O_2$. In addition, experiments with the mixed isotope $^{16}O^{18}O$ molecule, which did not show splitting of the band of the stretching vibration of $^{16}O-^{18}O$, indicated its lateral coordination. In similar experiments with CoTPP, the authors[11] showed terminal coordination, because two bands of stretching vibrations of the $^{16}O-^{18}O$ bond with splitting of 11 cm^{-1} were observed in the experiments with $^{16}O^{18}O$. These bands were assigned to two different molecules with $Co^{16}O^{18}O$ and $Co^{18}O^{16}O$ fragments.

The difference in the geometries of the O_2 complexes with CoTPP and MnTPP is also indicated by the fact that in the first case, on going from the argon matrix to the sublimed layer, the $\nu(O_2)$ frequency decreases[7] by 27 cm^{-1}, whereas in the second case, this decrease is only 5 cm^{-1}. This difference is close to the high-frequency shifts of the bands that are usually observed on going from molecules in the associated state to matrix-isolated molecules.[6] It is reasonable to assume that the dioxygen coordinated through one of the atoms is prone to a stronger influence of intermolecular interactions in the layer.

Along with the difference between the geometries of the complexes, the coordination of O_2 with the sublimed MnTPP layers possesses several specific features, which distinguish it from coordination in the sublimed CoTPP layers.[7] A sufficiently narrow temperature interval is used for investigations by the matrix isolation techniques for spectrally studying thermally unstable adducts.[11] The high microporosity of the low-temperature MTPP sublimates makes it possible to prepare and study unstable complexes without restrictions to the temperature interval of the study.

For example, the removal of O_2 from the CoTPP · O_2 adduct already at the temperature of liquid nitrogen results in a slow decomposition of the complex, which is indicated by a decrease in the intensity of the band of stretching vibrations of the O—O ($^{18}O-^{18}O$) bonds of the coordinated dioxygen at 1251 (1184) cm^{-1}. An increase in the temperature of the sublimed layer by several tens of degrees increased considerably the rate of this process. The coordination is reversible because the supply of a new dioxygen portion on the sublimed layer reproduces the spectral pattern induced by the first supply.

In the case of MnTPP · O_2, the many-hour evacuation (in a high vacuum) at 77 K does not noticeably decrease the intensity of the $\nu(O_2)$ band at 978 cm^{-1}. Thus, the oxygen MnTPP complex is thermally more stable than that with CoTPP. However, IR spectral control showed that the removal of the coordinated O_2 by evacuation at elevated temperatures (~200 K) and the supply of a new portion of O_2 results only in a partial increase in the intensity of the band at 978 cm^{-1}, *i.e.*, dioxygen coordination by the sublimed MnTPP layer is not completely reversible. This is also indicated by the electronic absorption spectra of the sublimed layer (see Fig. 2). The incomplete reversibility of this process was also observed in low-temperature solutions.[4]

The detailed study of the vibrational spectra explains in part this behavior. Unlike CoTPP, the coordination of O_2 with the MnTPP complex considerably reflects the vibrational spectrum of the porphyrin itself. The formation of the adduct with O_2 somewhat changes the character of the band splitting in the spectrum due to a decrease in the symmetry of the complex from D_{4h} to C_{2v}.[6] In addition, the spectrum exhibits new effects, which are undoubtedly related to a change in the oxidation and/or spin states of the metal atom.

The sensitivity of several bands in the IR spectrum to a change in the oxidation and spin states of the metal has previously[12,13] been found for the penta- and hexacoordinated FeTPP complexes with N-, O-, S-, and C-donating ligands. As the data of the present and previous works[14] show, Mn porphyrinates are other examples of this kind. In our opinion, this is due to the closeness of the energies of the d_π-orbitals of the metal and π-orbitals of the porphyrin for the Fe and especially Mn complexes. Precisely this explains[15] the uniqueness of the absorption spectra of Mn^{III} porphyrinates. The interaction of the π-orbitals of the porphyrin with the d-orbitals of the metal, which is virtually absent from porphyrinates of other transition metals because of a high difference in energies, results, in the case of Fe and Mn porphyrin complexes, in the situation where the electron effects related to the axial coordination can directly reflect the electron density distribution in the macrocycle. As a result, some normal vibrations of the macrocycle can manifest a noticeable sensitivity to the nature of the axial ligand and the character of coordination with the metal atom.

The frequency of the stretching vibration of the coordinated dioxygen in the adduct with MnTPP is closest to the value that characterizes its peroxide state. The high-spin state of Mn$^{\rm IV}$ in the adduct is also favored by the ESR data.[4] Therefore, it should be assumed that the Mn$^{\rm IV}$TPP $\cdot$ $O_2{}^{2-}$ complex forms, although the absorption spectra of the adduct are close to those of Mn$^{\rm III}$ porphyrinates.[4]

The bands at 1350, 800, and 450 cm^{-1} marked[12,13] for FeTPP have the same sensitivity in the case of MnTPP as well. The positions of the band in the region of 1350—1330 cm^{-1} attributed predominantly to $\nu(C_{mezo}{-}C_{Ph})$[16] and the band in the region of 469—432 cm^{-1} that characterizes low-energy deformation vibrations of the porphyrin skeleton[12] change with a change in the spin state of the iron ion. For the high-spin complexes, they are in the low-frequency regions of the marked intervals, whereas for the low-spin complexes, they lie in the high-frequency regions. On going from MnTPP to Mn$^{\rm IV}$TPP $\cdot$ $O_2{}^{2-}$, a combined band at 1333 and 1337 cm^{-1} is transformed into a single band with a maximum at 1346 cm^{-1}, and a band at 428 cm^{-1} is shifted to 455 cm^{-1} (Fig. 3), *i.e.*, the shifts have the same character as those observed for the Fe porphyrinate on going from the high- to low-spin state. Taking into account that the metal in the Mn$^{\rm IV}$TPP $\cdot$ $O_2{}^{2-}$ complex exists, most likely, in the high-spin state,[4] the observed high-spin shift of the bands marked can be explained as follows.

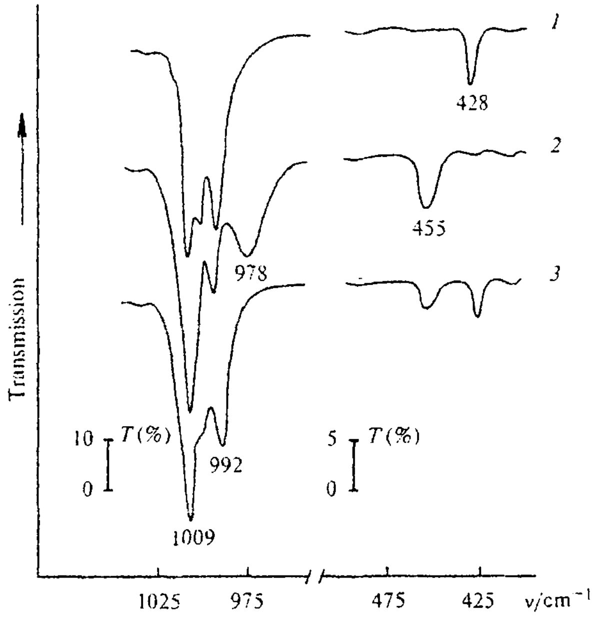

Fig. 3. IR spectra of the sublimed MnTPP layer at 80 K before (*1*) and after O_2 supply to the cryostat (*2*) and its evacuation in a high vacuum at 200 K for 1 h (*3*).

The Mn$^{\rm II}$ porphyrinates represent d^5 systems, whereas the Fe$^{\rm II}$ porphyrinates contain six d-electrons. Thus, in the case of transition to the Fe$^{\rm III}$ state, the iron ion still contains five d-electrons, and in the high-spin state the $d_{x^2-y^2}$-orbital with lobes directed to the pyrrole N atoms remains half-filled. The situation is different for Mn$^{\rm III}$ and the more so for Mn$^{\rm IV}$. This orbital is unoccupied even in the high-spin state, which favors the overlapping of the π-orbitals of the macrocycle with the d_π-orbitals of the metal. Therefore, it becomes clear that these bands behave similarly during spin transitions in the case of both Fe$^{\rm II}$ and Fe$^{\rm III}$ porphyrinates. From the viewpoint of filling of the $d_{x^2-y^2}$-orbital, the oxidation of Mn$^{\rm II}$ porphyrinates is equivalent to the transition to the low-spin state. These considerations allow the observed shifts of the bands in Fe and Mn porphyrinates to be explained from the single point of view.

The band in the region of 806—790 cm^{-1}, which was assigned to nonplanar deformational vibrations of the porphyrin macrocycle[7] on the basis of the orientation and polarization, is sensitive to the oxidation state of the iron ion.[6] In the case of MnTPP, as for FeTPP, this band undergoes a high-frequency shift from 798 to 802 cm^{-1}. Thus, the electronic structure of the porphyrin considerably changes due to the coordination with O_2. Similar changes in the IR spectra were also observed on going from MnTPP to the nitrate complex Mn$^{\rm III}$TPP $\cdot$ $NO_3{}^-$.[14]

The IR bands indicated can serve as good spectral markers to reveal the state of the metal ion in the axial MnTPP complexes. The arrangement of these bands in the low-frequency region of the intervals presented indicates the high-spin state of Mn$^{\rm II}$ in the complex. The band at 428 cm^{-1}, which is comparatively intense for the low-frequency spectral region, is especially convenient for these purposes. Its shift on going from Mn$^{\rm II}$ to Mn$^{\rm III}$ and Mn$^{\rm IV}$ or, in an unchanged oxidation state of manganese, to a state with a decreased multiplicity (according to our measurements, in the low-spin nitrosyl MnTPP $\cdot$ NO complex,[17] this band also appears at 455 cm^{-1}) is accompanied by considerable high-frequency (more than 25 cm^{-1}) shift of this band.

Prolonged evacuation of the sublimed MnTPP layer containing the dioxygen complex at 200 K removes the coordinated dioxygen (the $\nu(O_2)$ band at 978 cm^{-1} disappears completely). However, the IR spectrum of the sample subjected to this procedure does not reproduce that of the initial MnTPP layer. Although the intensity of the structure-sensitive bands observed for the Mn$^{\rm II}$ state increases, it does not reach the initial value, which is clearly demonstrated in Fig. 3 for the low-frequency band at 428 cm^{-1}. The supply of a new portion of O_2 at the liquid nitrogen temperature even at higher pressures of the latter results in the coordination of considerably smaller amounts of O_2. The spectral data indicate that this is precisely the portion of the Mn$^{\rm II}$

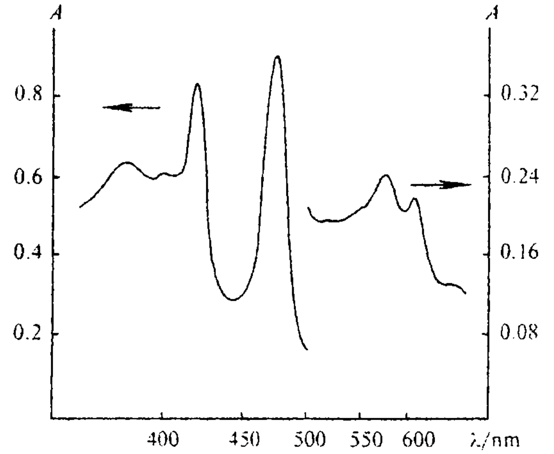

Fig. 4. Absorption spectrum of the sublimed MnTPP layer after its exposure to O_2 for 16 h followed by dissolution in CCl_4.

porphyrinate remaining in the layer which coordinates with O_2. Thus, some molecules in the layer are irreversibly oxidized already due to the first O_2 supply and heating the adduct to 200 K.

Exposure of the low-temperature MnTPP sublimate in the O_2 atmosphere to elevated temperatures leads to its irreversible oxidation. The absorption spectrum of the substance taken from the support and dissolved in CCl_4 contains two intense bands (Fig. 4). One of them, at 420 nm, is characteristic[18] of the O=MnTPP manganyl complex, whereas the second band with a maximum at 476 nm and the accompanying band at 380 nm are typical of the spectra of Mn^{III}TPP and belong, most likely, to its μ-oxo dimer.[15]

It should be mentioned in conclusion that O_2 coordination is observed only for MnTPP layers obtained by sublimation on the low-temperature surface. Upon dioxygen supply, the layers obtained by sublimation on the surface at room temperature and then cooled to 77 K do not exhibit spectrally detectable amounts of coordinated O_2. The MTPP molecules in these layers are predominantly parallel to the support plane,[19] creating unfavorable conditions for oxygen diffusion into the layer bulk followed by its coordination.

Experimental

IR spectra were obtained on a Specord M-80 spectrophotometer and a Perkin—Elmer 1600 FTIR spectrometer. The spectral width of the gaps was 4 cm^{-1}. Electronic absorption spectra were recorded on a Specord M-40 spectrophotometer.

Since Mn^{II} porphyrinates are very sensitive to air oxygen and readily transformed into Mn^{III} derivatives, more stable MnTPP·B complexes with nitrous bases (B is pyridine or piperidine) were used. They were synthesized by the known procedure.[10] Then the low-temperature sublimate was prepared.[6] The MnTPP·B sample was placed in a Knudsen cell and heated to ~480 K in a high vacuum. Evacuation for 3 h resulted in the elimination of the coordinated axial ligand B, which was monitored by measurement of the vacuum at the outlet of the cryostat. Then liquid nitrogen was poured in the cryostat, and the temperature of the heater was increased to ~530 K, at which sublimation was carried out. To obtain layers with a thickness convenient for IR spectral studies, sublimation was carried out for ~3 h, and for recording electronic spectra, sublimation took several min (in the region of the Soret band) and several tens of min (for bands in the visible region). Thoroughly dried and pre-cooled dioxygen was slowly fed to the cryostat from a vessel provided with a mercury manometer to measure the equilibrium pressure of O_2.

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