Structural features of sublimed layers of *meso*-mono-4-pyridyltriphenylporphyrinatocobalt(II) and reversible binding of molecular oxygen

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The interaction of oxygen with sublimed layers of *meso*-monopyridyltriphenylporphyrinatocobalt(II) (CoMPyTPP) was studied by electronic absorption and IR spectroscopy. The reversible binding of O_2 to the axial 5-position was shown for the freshly sublimed layers: the 6-position can either be free, or occupied by the pyridyl group of the adjacent molecule in the layer. The concentration of the complexes of the first type decreases to zero with time, whereas that of the second type complexes increases. The binding of oxygen on the sublimed layers of CoMPyTPP differs substantially from that on *meso*-tetraphenylporphyrinatocobalt(II) and *meso*-tetra-3(4)-pyridylporphyrinatocobalt(II), which loose their capability of O_2 binding with time.

Key words: *meso*-monopyridyltriphenylporphyrinatocobalt(II), sublimed layers, oxygen binding, IR spectroscopy, electronic absorption spectroscopy.

The capability of chelate Co^{II} complexes of oxygen binding evoked an interest to search for the systems, which retain the capability of oxygen fixation for a long time.[1] Some metalloporphyrins are known as efficient oxygen carriers and promising adsorbents of oxygen,[2] artificial hemoglobin,[3] and oxygen-permselective membranes.[4]

Thin porphyrin layers can be used in photovoltaic cells,[5] gas sensors,[6] and heterogeneous catalytic systems.[7,8]

The studies of sublimed layers of cobalt(II) *meso*-tetraphenylporphyrinate (CoTPP)[9] and structurally similar cobalt(II) *meso*-tetra-4(3)-pyridylporphyrinates (CoT4PyP and CoT3PyP)[10,11] showed that on storing at room temperature the films loose the ability to bind O_2. According to the spectral data, the CoT4PyP and CoT3PyP layers slowly loose the ability to bind oxygen because they form saturated complexes with coordination number 6 due to the interaction of the metal ions with the pyridyl groups of adjacent molecules. It could be expected that a decrease in the number of pyridyl groups in the *meso*-positions of the porphyrin macrocycle decreases the probability of formation of these structures and improves the oxygen-binding affinity of the layer.

In this work, we synthesized cobalt(II) *meso*-mono-4-pyridyltriphenylporphyrinate (CoMPyTPP) and studied the ability of its sublimed layers obtained under different conditions to bind oxygen.

Experimental

CoMPyTPP samples were synthesized using the method of mixed aldehydes.[12] Sublimed layers were obtained on supports of an optical cryostat, which were stored at either 77 K or room temperature according to a published procedure.[9]

To obtain the layers with a thickness convenient for IR spectral studies, sublimation was performed for ~3 h, and for recording electronic absorption spectra (EAS), it took up to tens of min. Thoroughly dried and pre-cooled oxygen was slowly fed to a cryostat from a vessel attached to a mercury gauge for measurements of the O_2 pressure (~60 Torr at temperatures of the support near the temperature of liquid nitrogen). Then the sublimed layer was stored for 30 min while the temperature was alternated in the following sequence: 80 → 120 → 80 K, oxygen was pumped out, and electronic or IR spectra were recorded.

IR spectra were recorded on a Specord M-80 spectrophotometer. The spectral width of the gaps was 4 cm^{-1}. Electronic absorption spectra were measured on a Specord M-40 spectrophotometer.

Results and Discussion

Figure 1 presents the IR spectra of the CoMPyTPP layer recorded after this layer was first sublimed on a support cooled with liquid nitrogen and then stored at 60 Torr O_2. As can be seen in Fig. 1, introduction of O_2 results in the appearance of two new absorption bands at 1250 and 1167 cm^{-1}. After the support was heated to room temperature, both bands disappear and the initial spectrum is restored. On admission of new portions of O_2, these bands appear again, but the intensity of the low-frequency band increases at the expence of the high-frequency band. Introduction of O_2 on the layer stored for 1 day at room temperature gives the spectrum with the band at 1250 cm^{-1} decreased and with the band

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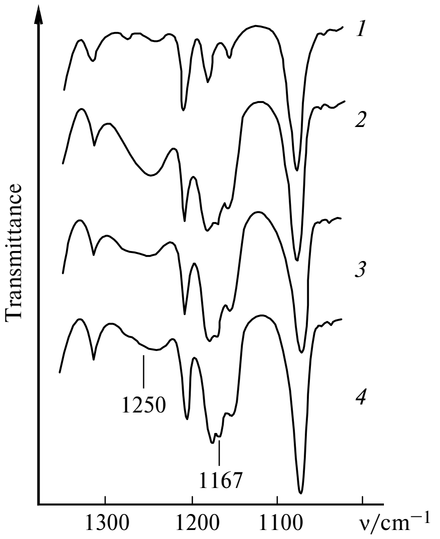

Fig. 1. IR spectrum of the sublimed CoMPyTPP layer at 80 K in the $\nu(O_2)$ region of coordinated oxygen (*1*); after oxygen admission into the cryostat (60 Torr), cyclic temperature change (80 → 120 → 80 K), and pumping out of a oxygen excess (*2*); after the same procedure performed in 1 day (*3*); and after the same procedure with the layer obtained by sublimation on the surface stored at room temperature (*4*).

at 1167 cm^{-1} substantially increased in intensity. At the first admission of O_2 on the layer obtained by porphyrin sublimation on the surface at room temperature, the intensity of the high-frequency band decreases (see Fig. 1, curve *4*).

Introduction of O_2 into the sublimed CoMPyTPP layer also changes EAS: both the Soret band and the band in the visible region experience the bathochromic shift (Fig. 2).

These results can be interpreted as follows. The reversible nature of binding of oxygen by the sublimed CoTPP layers has been shown previously.[9] The band at 1250 cm^{-1} was attributed to $\nu(O_2)$ of the $O_2 \cdot$ CoTPP adduct, and the assignment was confirmed by experiments with $^{18}O_2$. In similar experiments with the pyridyl-substituted derivatives of CoT4PyP [10] and CoT3PyP,[11] the $\nu(O_2)$ bands of bound oxygen appeared at 1160 cm^{-1}, and the adducts obtained were much more thermostable than those produced with CoTPP. These differences were explained in terms of the outer-sphere coordination of the pyridyl fragment of one porphyrin molecule with the cobalt ion of the adjacent complex and formation of five-coordinated complexes. Thus, the new bands found in this work for CoMPyTPP can unambiguously be assigned to oxygen complexes of two types: **A** and **B** (Fig. 3). In the Raman spectra of the six-coordinated $O_2 \cdot$ CoTPP $\cdot$ B complexes (B is the nitrogen base), the $\nu(O_2)$ band of coordinatively linked oxygen is also observed in the region of 1260 cm^{-1}.[14]

In the EAS of the sublimed CoMPyTPP layer (see Fig. 2, curve *1*), the Soret band is much broader and shifted to low frequencies compared to that of CoTPP,[11] although the chemical structures of these compounds are similar. The replacement of the CH fragment in one of the phenyl groups by N, under the conditions where the phenyl (pyridyl) ring is not coplanar with the porphyrin macrocycle, would not affect substantially the electron levels of the chromophore. Therefore, the marked spectral distinctions are presumably related to the composition of the sublimed CoMPyTPP layer with incorporated structures differed in the number of axial ligands (0, 1, 2) attached to the cobalt ion. Such structures can be formed only with pyridyl groups of adjacent molecules, especially since the shift of the bands is detectable in the EAS upon axial ligation.[15] Thus, the observed broadening of the Soret band can be attributed to the superposition of absorption bands shifted relatively to each other.

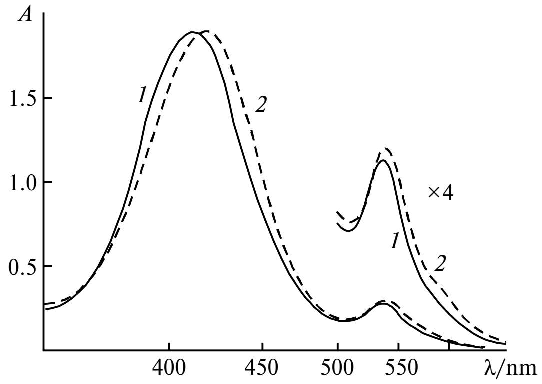

Fig. 2. Electronic absorption spectrum of the sublimed CoMPyTPP layer at 77 K before oxygen admission (*1*) and after oxygen admission into the cryostat (60 Torr), cyclic temperature change (80 → 120 → 80 K), and pumping out of a oxygen excess (*2*).

Exposure of the sublimed layer to oxygen results in the bathochromic shifts of both the Soret band and bands in the visible region. A low value of these shifts and a significant half-width of the observed bands impedes the discrimination between contributions made to the EAS by the adducts with different IR characteristics.

The sublimed CoMPyTPP layers show better affinities to bind oxygen than the CoTPP,[9] CoT4PyP,[10] and CoT3PyP [11] layers. Upon storage at room temperature for 1 month, the amount of bound oxygen estimated from the intensity of the $\nu(O_2)$ band at ~1160 cm^{-1} decreases by less than 20%, whereas the layers of CoT4PyP and CoT3PyP stored *in vacuo* for a week lost a half of the oxygen bound. The capability of CoMPyTPP of coordinating with oxygen is also retained for the layers stored in air. In similar experiments with the tetrapyridyl-substituted derivatives, the layers lost their ability to retain oxygen and the spectral data indicate the irreversible oxidation of Co^{II} to Co^{III} [11] caused, most likely, by the incorporation into the layer the bridging oxygen molecule ~Py $\cdot$ CoTPyP $\cdot$ O—O $\cdot$ CoTPyP $\cdot$ Py~.

The distinctions in the coordination power of sublimed layers of the compounds with similar structures are related to the features of their supramolecular structure. Crystals of metal *meso*-tetraphenylporphyrinates (MTPP) contain pores formed by narrow long channels[13] passing through the positions axial to the metal ions, and accessible for reactants. This was clearly demonstrated for the

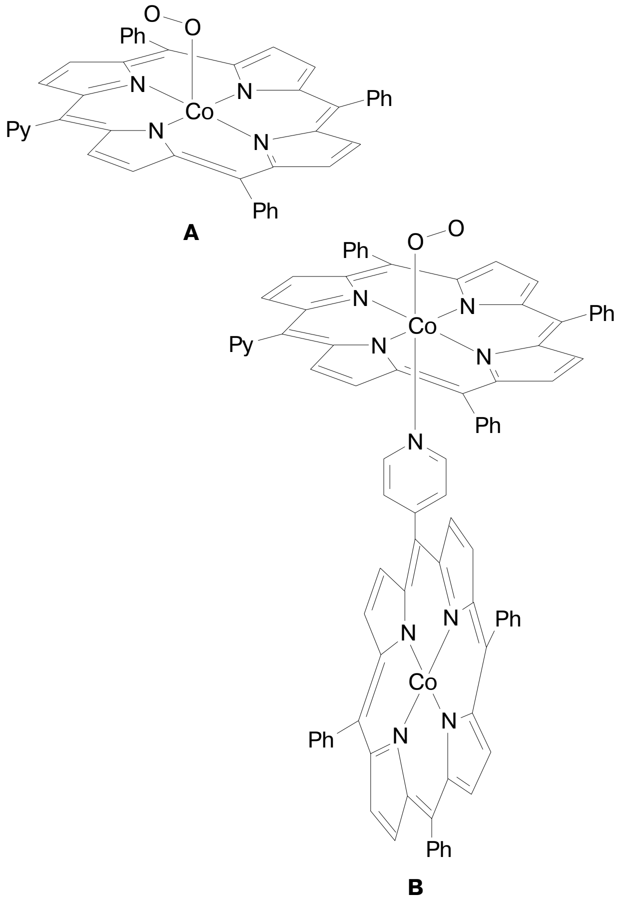

Fig. 3. Schematic view of the oxygen complexes in the sublimed CoMPyTPP layer.

out-of-sphere coordination of several ligands,[17,18] including O_2,[9] by the MTPP molecules over the whole volume of the low-temperature sublimate.

When MTPP are isolated from solutions, pores are usually filled with solvent or ligand molecules. If the pores remain unfilled, the cross section of the pore apertures is narrowed drastically[13] to hamper reactant diffusion into the channels inside the layer. Evidently, that is why the CoTPP layers stored at room temperature cannot bind O_2.[9]

When metalloporphyrin molecules contain functional substituents prone to initiate specific intermolecular interactions (hydrogen bonds, coordination, *etc.*), the solid state structures can show substantial changes.[18—20] In particular, the presence of pyridyl groups in the *meso*-positions of the porphyrin rings can result in the formation of oligomers and polymers due to the out-of-sphere coordination of one porphyrin molecule with the metal ion of the adjacent molecule.[21] For the 4-pyridyl-substituted derivatives, this coordination results, most likely, in the formation of much larger pores[21] than those in the compact MTPP structures.

As our experimental data show, the sublimed CoMPyTPP layers contain supramolecular structures of both types. This system is thermodynamically non-equilibrated and transformed with time into a more stable system in which five-coordinated CoMPyTPP molecules prevail. Due to the predomination of phenyl groups in the *meso*-positions, the probability of formation of six-coordinated saturated structures is low. The mutual perpendicular arrangement of the adjacent molecule makes improbable the formation of structures with the bridging oxygen group capable of irreversible metal oxidizing. For this reason, the property of the CoMPyTPP layers to bind oxygen persists on storing in air.

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