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Статья

Low−Temperature Interaction of Dioxygen and Carbon Monoxide with Microporous Films of Co(II) Porphyrins Containing Bulky tert−Butyl Substituents

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The low-temperature interaction of O_2, CO and their mixtures with sublimed layers of Co(II) complexes of 5,10,15,20-tetrakis(3',5'-di-tert-butylphenyl)porphyrin (**I**) and 5-(pyridin-4'-yl)-10,15,20-tris(3',5'-di-tert-butylphenyl)porphyrin (**II**) has been studied by FTIR and optical spectroscopy. In contrast to the layers of [5,10,15,20-tetraphenylporphyrinato]cobalt(II) Co(TPP), that lose their porosity and ligand-binding ability upon standing at ambient conditions overnight, the films of **I** conserve these properties for a long time. Thus the bulky tert-butyl groups of **I** substantially slow down the close packing of molecules in the films making metal ions accessible to different ligands. It is shown that the films of **II** consist of coordination oligomers, the sixth coordination site of which is occupied by the pyridyl group of an adjacent molecule in the film. The reaction of O_2 gas with these films leads to the formation of two types of complexes: six-coordinate dioxygen complexes, in which the fifth site is occupied by the pyridyl group of the neighboring molecule in the film and the five-coordinate dioxygen complexes that terminate the oligomers. Upon storage of the films, the concentration of six-coordinate complexes increases at the expense of the five-coordinate indicating increasing degree of oligomerization. In contrast, only the end group of oligomers is able to coordinate carbon monoxide CO. No six-coordinate complexes of CO with trans pyridyl group are formed in the films of **II** and the 6-coordination sites of oligomers remain free. When CO/O_2 mixture is admitted into the cryostat with films of **II** these sites selectively bind O_2. This phenomenon allows eliminating O_2 from the CO/O_2 mixture containing very low concentrations of O_2 and can be used for CO purification of trace quantities of dioxygen.

Keywords: Microporous metalloporphyrin films, Co porphyrins, bulky meso-substituents, coordination oligomers, O_2 and CO adducts, FTIR and optical spectra, gas separation, low temperatures.

Взаимодействие кислорода и монооксида углерода с микропористыми пленками Co(II) порфирина с объемными трет−бутильными заместителями при низких температурах

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*Методами Фурье-ИК и электронной абсорбционной спектроскопии исследовано низкотемпературное взаимодействие двухатомных молекул (O₂, CO) и их смесей с пленками 5,10,15,20-тетракис(3',5'-ди-третбутилфенил)порфирината кобальта(II) (**I**) и 5-(пиридин-4'-ил)-10,15,20-трис(3',5'-ди-третбутилфенил) порфирината кобальта(II) (**II**), полученными сублимацией металлокомплексов в высоком вакууме. В отличие от слоев мезо-тетрафенилпорфирината кобальта(II) (CoТФП), быстро теряющих свою микропористость при хранении в вакууме при комнатных температурах, слои **I** сохраняют свою микропористость в течение продолжительного времени. Наличие объемных трет-бутильных заместителей в значительной степени замедляет процесс уплотнения пленок и при исследовании обратимых сорбционных процессов одна и та же пленка может быть использована многократно. Показано, что слои **II** состоят из координационных олигомеров, в которых пиридильная группа одной молекулы координируется с ионом Co соседней молекулы в слое. Степень олигомеризации зависит от условий получения и заметно выше в пленках, полученных сублимацией на подложку, поддерживаемую при повышенных температурах, по сравнению со слоями, осажденными на низкотемпературную поверхность. Сравнением полученных данных с теми же для пленок **I** выявлено, что в пленках **II** кислород образует два типа комплексов – 5-координационных в конце олигомерной цепи и 6-координационных в остальных звеньях. В последних в качестве шестого лиганда выступает координированная пиридильная группа соседней молекулы в пленке. Моноксид же углерода координируется исключительно в конце олигомера, оставляя шестое координационное положение в олигомерах свободным. При подаче в криостат с пленкой **II** смеси CO/O₂ эти положения селективно связывают O₂. Это дает возможность удалить кислород из газовых смесей CO/O₂ с малым его содержанием и, тем самым, очистить CO от следовых количеств кислорода.*

Ключевые слова: Микропористые пленки, координационные олигомеры, порфиринаты кобальта(II), объемные периферийные заместители, Фурье-ИК, электронная абсорбционная спектроскопия, координация O₂ и CO, низкие температуры.

Introduction

The construction of microporous materials containing metal ions in their network is an attractive tool for tailoring materials with useful chemoresponsive properties.[1-3] Metalloporphyrins are exclusively convenient molecules for acting as a building blocks for the construction of different microporous solids, since countless derivatives can be obtained by variation of the nature of the central metal ion and by inclusion of the various substituents in the periphery of the molecule.[4-6]

Thin films of porphyrin-like compounds have gained much interest as field and chemo-responsive materials because of their potential application in gas-sensing devices, selective adsorbents, heterogeneous catalytic systems, *etc*.[7-10] Some metalloporphyrins, including Co-derivatives, are also efficient oxygen carriers and have been studied for potential application as oxygen adsorbents, artifitial hemoglobin and oxygen-permoselective membranes.[11-13] In order to generate the films with useful properties, it is desirable to create porous systems in which not only surface molecules but also those in the bulk of layer would be active. It has previously been shown that the layers of *meso*-tetraphenylporphyrinatocobalt (CoTPP), obtained by sublimation on the low-temperature substrate are microporous and reversibly bind dioxygen.[14] However, upon storing at ambient conditions they lose this ability due to close packing of the molecules in the layer thereby inhibiting the diffusion of gaseous molecules in the bulk of layer.

We proposed that the presence of bulky *tert*-butyl groups in the periphery of molecules will prevent close packing of the molecules in the films or at least will slow down the rate of this process, so the same film would conserve its porosity longer and could be used repeatedly. In this paper we describe the studies of O₂ and CO interaction with sublimed films of **I** and **II**, in which we found that the films of **II** reveal some specificity in binding of these ligands and can be used for purification of CO/O₂ mixtures of trace amounts of O₂.

Experimental

Metal free 5-(4-pyridin-4-yl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin was synesized by the condensation of 4-pyridinecarboxaldehyde (1 eq.), 3,5-di-*tert*-butylbenzaldehyde (3 eq.) and pyrrole (4 eq.) in propionic acid according to the documented procedure.[15] Symmetrical metal free 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin was obtained as co-product. Co(II) complexes **I** and **II** were prepared from free ligands by reflux with cobalt acetate in DMF. Porphyrins **I** and **II** were purified through a column of Al₂O₃ and eluted with CHCl₃-MeOH (100:0.5) mixture.

The Co-porphyrins **I** and **II** were placed in the Knudsen cell and heated up to ~450 K under high vacuum for the removal of the solvated molecules. Then the cryostat was filled with liquid nitrogen and the temperature of the Knudsen cell was raised up to ~500 K and 550 K for **I** and **II** correspondingly, where these metal complexes were sublimed onto a KBr (for FTIR measurements) or CaF₂ (for UV-visible measurements) substrates. The films of **II** were obtained also by sublimation onto substrates, maintained at room temperature or heated to 323 K. In order to obtain layers with thicknesses suitable for infrared and UV-visible measurements, the deposition was performed for 1.5–2 and 0.5 hours respectively. Molecular oxygen was stored in cylinders with P₂O₅ for the removal of the trace amounts of moisture.¹⁸O₂ gas was with 95 % enrichment was acquired from the Cambridge isotopic laboratories, C¹⁸O with 81.4 % enrichment from the Institute of isotopes, Republic of Georgia.

The layers of **II** obtained via sublimation onto a low temperature substrate were heated up to room temperature and kept in vacuum overnight. Different quantities of O₂, CO or their mixtures controlled by mercury monometer or by thermocouple gauge were then introduced into the cryostat at LN₂ and annealed

to assist the formation of complexes. The layer was then slowly warmed to room temperature and the FTIR or UV-visible spectra were obtained at various controlled temperatures measured by a thermocouple. The UV-visible spectra were taken after the FTIR measurements of the same samples confirmed the identity of each species. The FTIR and UV-visible spectra were acquired on a Nexus (Thermo Nicolet Corporation) in the spectral range 400–4000 cm⁻¹ with a resolution 2 cm⁻¹ and Specord M-40 (Carl Zeiss, Jena) or Helios γ (Thermo Nicolet Corporation) spectrometers in the range of 350–900 nm, respectively.

Results and Discussion

The Interaction of O₂ and CO with Films of *I*

It was previously shown that similar to the matrix-isolated molecules of Co(TPP),[16] its layers, obtained by sublimation onto the low-temperature substrate, are also able to bind dioxygen O₂ and carbon monoxide CO.[14,17] However, during storage at ambient conditions overnight they lose this ability due to close packing of the molecules in the layer and dramatically decreased cross section of the pores that prevents the diffusion of potential ligands in to the bulk of layer.

Similarly to Co(TPP), sublimed layers of **I** (Scheme 1) also form dioxygen adduct upon low-temperature reaction with O₂ gas as is demonstrated by the FTIR spectral changes represented in Figure 1. New band in the vicinity of 1250 cm⁻¹ appears in the spectrum that overlaps the band of porphyrin itself drastically enhancing its intensity. When ¹⁸O₂ is used in the experiment this band is shifted to 1180 cm⁻¹. From the value of this isotopic shift, and by analogy with previous work,[18] these bands can be readily assigned to coordinated dioxygen in the adducts (**I**)(¹⁶O₂) and (**I**)(¹⁸O₂).

Low-temperature interaction of CO with the film of **I** leads to the appearance of two bands in the range of CO stretching frequency at 2131 and 2058 cm⁻¹, which shift to 2080 and 2011 cm⁻¹ when isotopic C¹⁸O is used in the experiments (see Figure 5). The band at 2058 (2011 for C¹⁸O) cm⁻¹ by analogy with the matrix-isolation study of Kozuka and Nakamoto[16] and our work with sublimed layers of Co(TPP)[17] should be assigned to the adducts (**I**)(CO) and (**I**)(C¹⁸O).
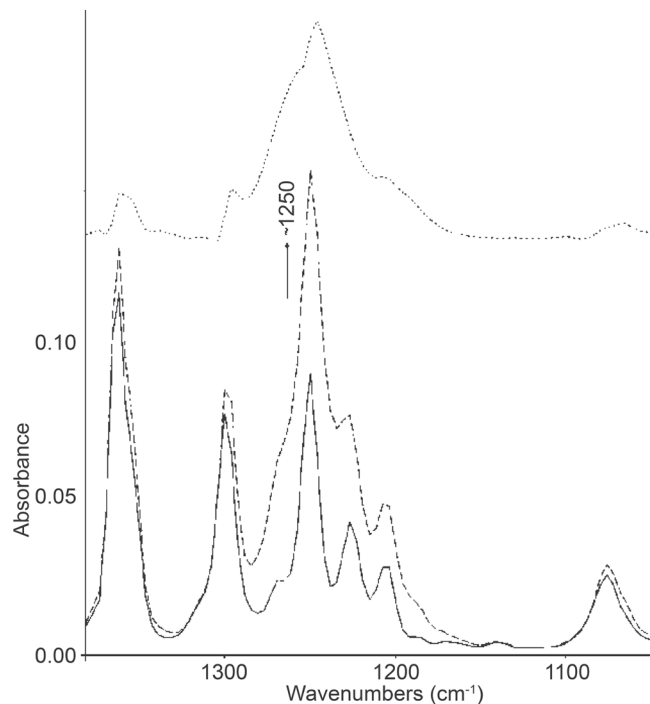

Figure 1. FTIR spectra of the film of **I** at 80 K (solid line) after exposure to 60 Torr O₂ and annealing in the cycle 80 K →120 K →80 K (dashed line) and difference spectrum (dotted line).

The high frequency band at 2031 (2080), previously observed upon CO interaction with the low-temperature microporous layers of Co(TPP) and assigned to the physically adsorbed CO,[17] must be of the same nature. Except for minor changes in the frequencies of absorption bands of coordinated ligands there are no principal differences regarding to interaction of these diatomics with the films of Co(TPP) and **I**, what is to be expected. Another thing is important. In contrast to the layers of Co(TPP), that lose their reversible ligand-binding ability already during storage overnight, the films of **I** remain active for a long time. The films, stored within two weeks at a room temperature showed decrease in the amount of coordinated oxygen only ~20 %. Thus, the process of close packing in the films is substantially slowed down due to the presence in their structure of *tert*-butyl bulky substituents.
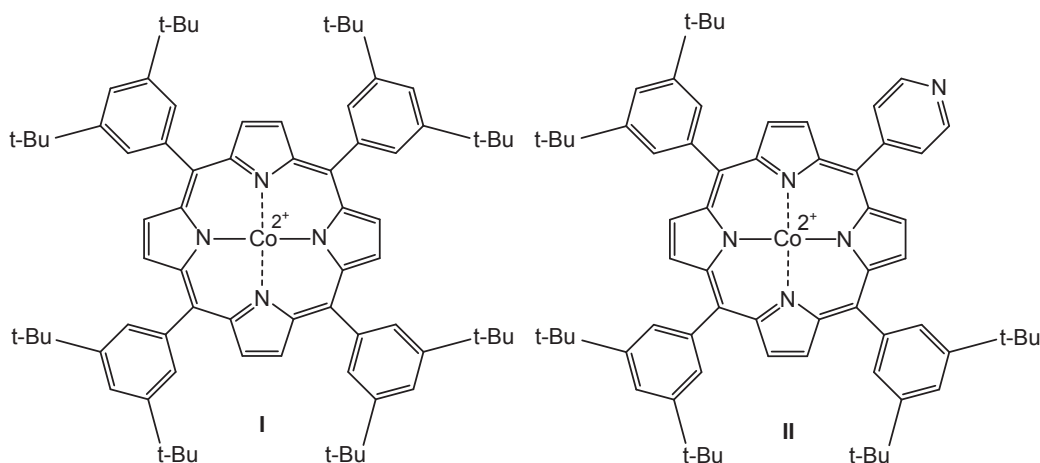
Scheme 1.

Thereby, in the studies of reversible processes the same film can be used multiple times that created a lot of flexibility and resulted in a saving of expensive material.

The Interaction of O₂ and CO with Films of *II*

Admission of O_2 gas into cryostat containing sublimed film of **II** leads to the FTIR spectrum represented in Figure 2. It reveals two new bands, one in the vicinity of 1250 cm⁻¹ analogous to that appeared for the film of **I** (see Figure 1) and assigned to the complex (**I**)(O₂) and another one at 1168 cm⁻¹. The same procedure with isotopically enriched $^{18}O_2$ shifts these bands to ~1180 and 1108 cm⁻¹ (Figure 2) correspondingly. This isotopic dependence confirms its assignment as a dioxygen stretching mode, and indicates the formation of another type of complex. After the support is heated to room temperature, both bands disappear and the initial spectrum is restored. On admission of new portions of O₂, these bands appear again, but the intensity of the low-frequency band increases at the expense of the high-frequency band.
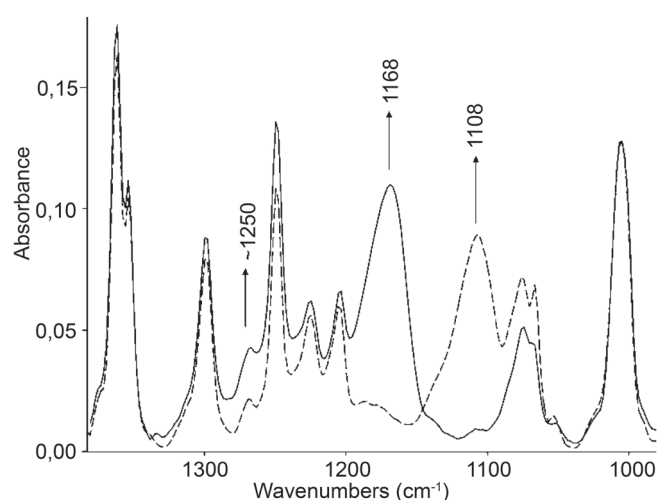

Figure 2. FTIR spectra of the film of **II** after exposure to 60 Torr O₂ and annealing in the cycle 80 K →120 K →80 K (solid line); the same in the presence of 6 Torr $^{18}O_2$ (dashed line).

The ratio of intensities of the low- and high-frequency bands depends on the conditions of film preparation. Upon storage of the films, the concentration of six-coordinate complexes increases at the expense of the five-coordinate species. It is also higher when during sublimation the substrate was maintained at higher temperatures (Figure 3).

The results obtained are very close to those observed for the films of Co(II) complex of 5-(pyridin-4-yl)-10,15,20-triphenylporphyrin (Co(M4PyTPP))[18,19] and explained in terms of formation of coordinatively linked oligomers and formation of a six-coordinate dioxygen adduct with the pyridyl base in the *trans* axial position. The same pattern was observed upon interaction of O₂ with sublimed layers of Fe(M4PyTPP).[20] Hence despite the presence of bulky tert-butyl groups the same type of oligomers (Scheme 2) is formed in the films of **II** too. The six-coordinate dioxygen complexes formed by oligomeric units are thermally much
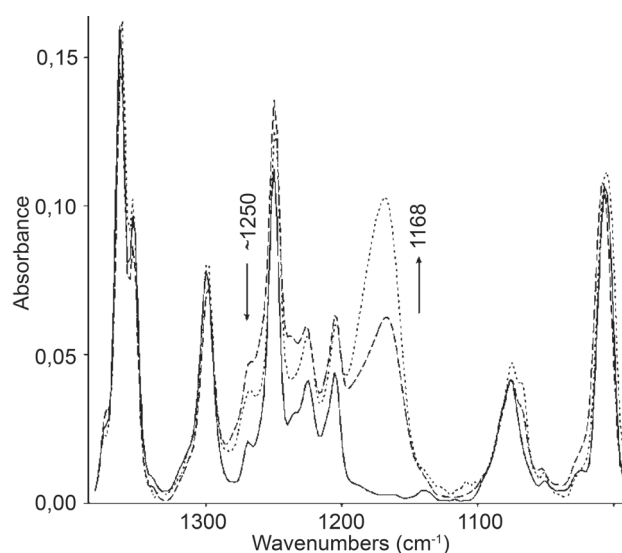

Figure 3. FTIR spectra of the film of **II** at 80 K in the range of O₂ stretching mode: initial spectrum (solid line) after admission of O₂ gas on the film obtained by sublimation onto the low-temperature (80 K) substrate (dashed line), after admission of O₂ gas on the film obtained by sublimation on the substrate, maintained at 323 K (dotted line).

more stable than five-coordinate dioxygen complexes that terminate the oligomers.

The electronic absorption spectrum of **II** also undergoes noticeable changes in the course of interaction with O₂. As seen in the Figure 4 the band of **II** in the visible range at 532 nm shifts to 534 nm and displays a shoulder at 588 nm upon formation of dioxygen complexes.

Thus the interaction of O₂ gas with the films of **I** and **II** is significantly different. At the same time the interaction of CO with these films leads to almost identical results with two bands in the range of CO stretching vibration. The high-frequency bands are close in frequency to the $\nu(CO)$ of gas phase (ν =2141 cm⁻¹) and matrix-isolated (ν =2137 cm⁻¹) CO and should be assigned to the $\nu(CO)$ of CO molecules adsorbed in films.[16] Upon films warming these bands
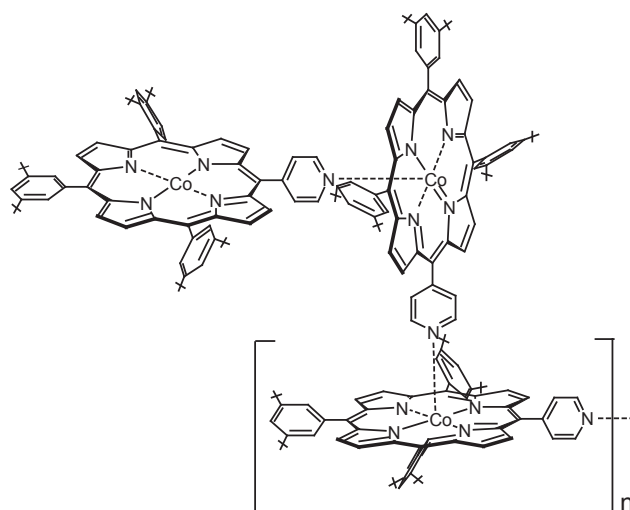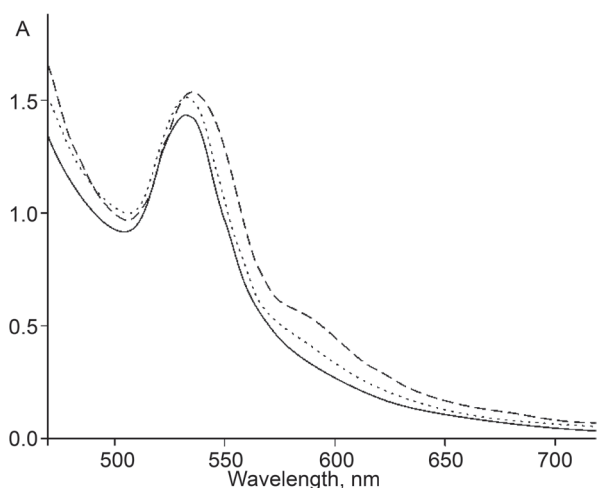

Scheme 2.

Figure 4. UV-visible spectra of **II** (solid line) after low-temperature interaction with O$_2$ (dashed line) and CO (dotted line). The spectra were taken after FTIR measurements of the same samples confirming the identity of each species.

Figure 5. FTIR spectra of the films of **I** (solid line) and **II** (dashed line) after exposure to 40 Torr CO and annealing in the cycle 80 K →120 K →80 K (solid line). Gas phase CO was pumped out at 80 K.

disappear first, indicating the low energy of CO binding. The low-frequency bands are close in frequency to each other and to the value of the ν(CO) in monocarbonyl complex Co(TPP)(CO) (ν=2066 cm^{-1})[16,17] and can be also assigned to monocarbonyl complexes. There is no any spectral feature indicating formation of the six-coordinate carbonyl complex with the *trans*-pyridyl group of neighboring molecule in the film.

It must not be ruled out, that coordination of CO could lead to the disruption of the bond between Co-ion and pyridyl group of an adjacent molecule, leading actually to the destruction of oligomeric structure in a film. In this case only formation of the 5-coordinate monocarbonyl complexes (**II**)(CO) should be expected. The closely related pattern took place in the course of interaction of the other diatomic molecule, NO, with the heme of the soluble guanylyl-cyclase, leading to disruption of the Fe-histidine bond, followed by enzyme conformation changes and its more than 200-fold activation.[21] Following experimental observation, however, excludes such possibility.

The equal quantities of CO were admitted into the cryostat with films of **I** and **II**. Using the intensities of the ν(CO) band the relative amounts of CO coordinated by these films were estimated. The intensity of band at about 1000 cm^{-1} was chosen as a reference. This band is present in all *meso*-tetra-aryl substituted porphyrins and their metal complexes and corresponds to the mixed δ$_{sym}$(C-C-C) + ν(Pyr. Breathing) + ν$_{asym}$(Pyr. Half-ring) mode.[21] Assuming in rough approximation that in the films of **I** and **II** these bands are approximately equal intensity, it can be concluded from the spectra of Figure 5 that the amount of coordinated CO in the films of **II** about three times less than in the film of **I**. Here we assume that substitution of one 3',5'-di-*tert*-butylphenyl ring by pyridyl ring should not significantly change the extinction coefficient of the coordinated CO moiety. It means in turn that only one third of molecules in the film of **II** coordinates CO molecules. This observation is in contrast with the assumption that CO coordination results in disruption of the
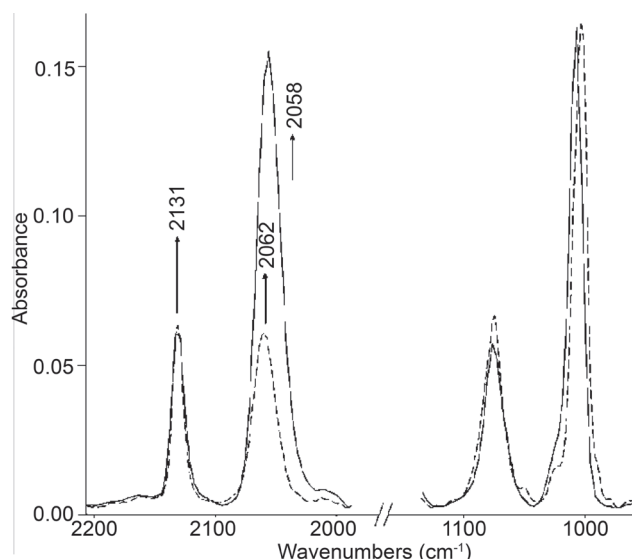
Co-pyridyl bond. From these data the circumstantial information about the degree of oligomerization can be obtained, which is equal to three in average.

Only minor changes are observed in the electronic absorption spectrum of the film of **II** after interaction with CO (Figure 4, dotted line). It is easy to understand since only small part of **II** is engaged in coordination with CO.

The absence of the 6-coordinated carbon monoxide complex with *trans* pyridyl ligand is not surprising. Hoffman and Petering did not find any evidence of such a complex formation upon interaction of one atmosphere CO with deoxy-coboglobin.[22] In this protein the proximal ligand was histidine. Moreover, studies on the model Co(P)-dimethyl ester (P-protoporphyrin-IX) in organic solvents containing nitrogen bases also fail to detect coordinated CO, as was demonstrated by ESR and optical absorption methods.[23]

As it was mentioned above the storage of the films of **II** leads to the increase of degree of oligomerization. It will affect the relative amounts of coordinated dioxygen and carbon monoxide. As seen in Figure 6, upon storage of the film of **II** under vapor of CO/O$_2$ mixture the amount of the 6-coordinate dioxygen adduct (band at 1168 cm^{-1}) increase at the expense of the coordinated carbon monoxide (band at 2064 cm^{-1}). This observation also indicates that CO is coordinated exclusively with the end group of oligomers (Scheme 3).

As it was noted above in the presence of CO the sixth coordination site of oligomers in the films of **II** remains free. Therefore upon supplying of a CO/O$_2$ mixture into cryostat these ligands do not compete for binding with those metal centers that included in oligomers. By this reason even very low quantities of O$_2$ in the mixture can be captured by the films of **II**. The Figure 7a represents the FTIR spectral changes accompanying the interaction of CO/O$_2$ mixture containing 10 Torr CO and 0.01 Torr O$_2$ with the film of **II**. The band ν(O$_2$) of the 6-coordinated dioxygen even at such low pressure is seen
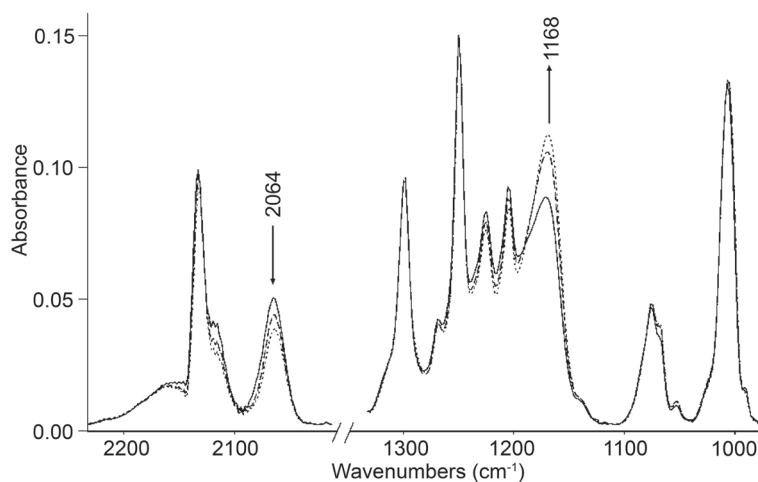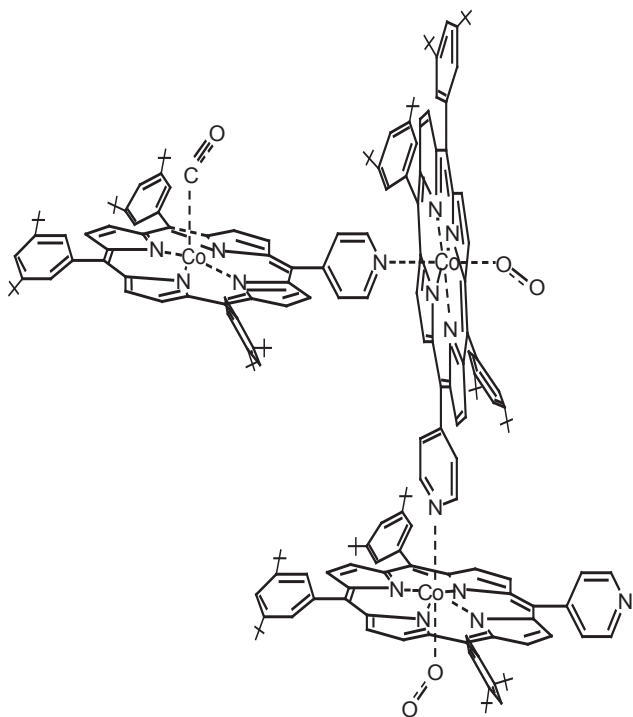
Figure 6. FTIR spectra of the film of **II** exposed to 15 Torr of O_2/CO (1:1) mixture and annealed in the cycle 80 K →120 K →80 K (solid line) after warming to 300 K and recooling to 80 K (dashed line) and after storage under O_2/CO atmosphere overnight (dotted line).

Scheme 3.

quite clearly, despite of the presence of large CO excess. At the same time interaction of CO/O_2 mixture with films of **I** even at higher pressure of O_2 and smaller ratio of CO/$^{18}O_2$ does not reveal detectable quantities of coordinated $^{18}O_2$ (Figure 7b). In this experiment the isotopic $^{18}O_2$ was used because the weak band of coordinated O_2 disposed in the vicinity of 1250 cm^{-1} could not be clearly seen due to the presence of the intense porphyrin bands in this spectral range. The $\nu(^{18}O_2)$ of coordinated $^{18}O_2$ is disposed in the 1180 cm^{-1} range free of the bands of porphyrin itself and should be clearly seen if such adduct is formed during reaction of CO/$^{18}O_2$ with **I**. Obviously upon reaction with films of **I** the competition between CO and O_2 ligands for the binding with vacant metal sites in conditions when CO>>$^{18}O_2$ would lead to the negligibly small quantities

of coordinated O_2 that could not be detected spectrally. The data obtained clearly show that the films of **II** preferentially bind dioxygen from the CO/O_2 mixture and can be used for their purification from trace amounts of O_2.

Conclusions

Sublimed layers of Co(II) complex of 5,10,15,20-tetrakis(3',5'-di-*tert*-butylphenyl)porphyrin (**I**), in contrast to the layers of [5,10,15,20-tetraphenylporphyrinato]cobalt(II) Co(TPP) that lose their porosity and ligand-binding ability upon standing at ambient conditions, conserve these properties for a long time. Obviously, the bulky *tert*-butyl groups of **I** slow down the close packing of molecules in the films making metal ions accessible to different ligands for a long period. As a result these films can be repeatedly used for various applications. The self-assembly of Co(II) complex of 5-(pyridin-4'-yl)-10,15,20-tris(3',5'-di-*tert*-butylphenyl)porphyrin (**II**) in sublimed layers leads to the formation of one-dimensional coordination oligomers, in which the pyridyl group of one molecule is coordinated with the metal ion of an adjacent molecule in the layer. The low temperature interaction of O_2($^{18}O_2$), CO (C^{18}O) and their mixtures with the films of **I** and **II** studied by FTIR and UV-vis spectroscopy shows that films of **II** reveal different binding properties in relation to these ligands. Both the 5- and 6-coordinate complexes are formed with O_2-ligand, the former at the end of oligomers and the latter with one coordination site occupied by the pyridyl group of an adjacent molecule, while only the end group of oligomers binds CO, forming exclusively 5-coordinate species. As a consequence the films of **II**, revealing different binding abilities in relation to O_2 and CO, can be used for practical purposes, particularly, for purification of CO/O_2 mixture from trace amounts of O_2.
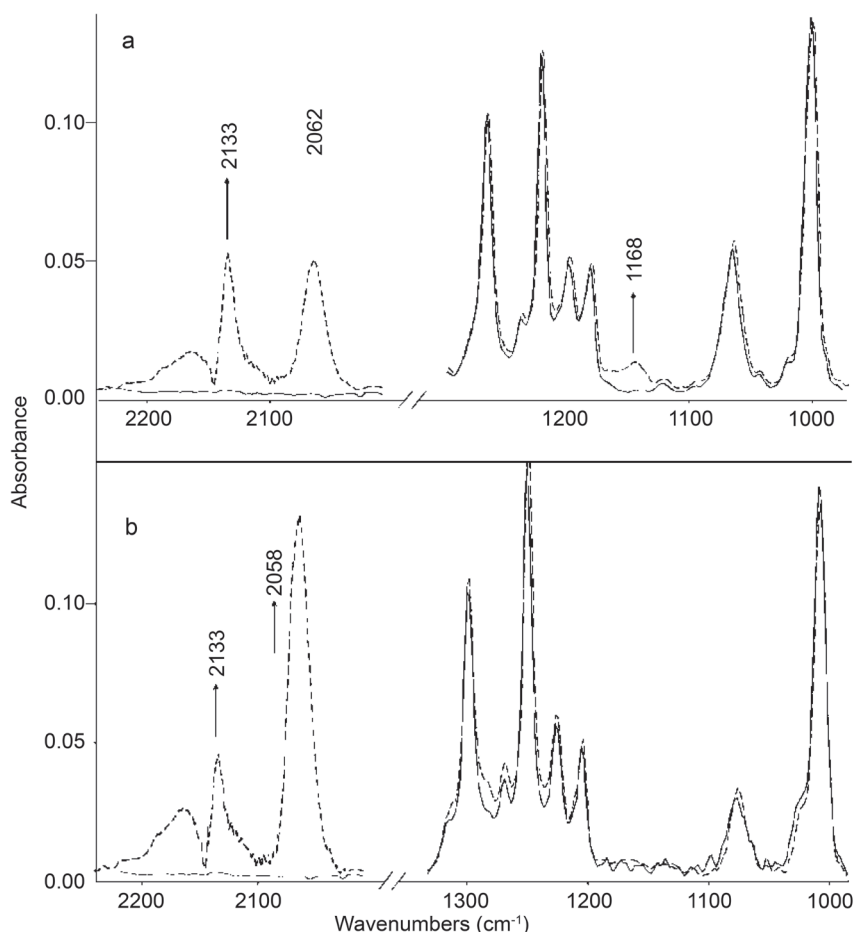
Figure 7. (a) FTIR spectra of the film **II** (solid line) after interaction with the gaseous mixture containing 10 Torr CO and 0.01 Torr of O_2 (dashed line); (b) FTIR spectra of the film **I** (solid line) after interaction with the gaseous mixture containing 15 Torr CO and 0.15 Torr of $^{18}O_2$ (dashed line). The mixtures was admitted into the cryostat at room temperature and cooled to 80 K. The broad band in the 2100–2200 cm^{-1} range is of the gas phase CO.

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