Carbon Monoxide Coordination by Iron(II) meso-Mono-4-Pyridyltriphenylporphyrinate (FeM4PyTPP) and Its Structure in Sublimed Layers

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Abstract—Interaction of CO with sublimed layers of iron(II) *meso*-mono-4-pyridyltriphenylporphyrinate (FeM4PyTPP) resulting in the formation of known mono- and dicarbonyl complexes was studied using IR spectroscopy. The frequency of the stretching vibration of the coordinated CO in the monocarbonyl complex was found to be ~20 cm⁻¹ higher than in the complex with iron *meso*-tetraphenylporphyrinate (FeTPP), with the former complex being significantly more stable than the latter. The differences observed in CO coordination by porphyrins with close structures are explained by the formation, in the FeM4PyTPP sublimed layers, of oligomeric structures where the pyridyl group of one molecule is coordinated by the metal ion of the neighboring molecule. This conclusion is confirmed by a comparative analysis of IR spectra of FeM4PyTPP and FeTPP in the regions of structurally sensitive vibrations.

Metal complexes of *meso*-pyridyl-substituted porphyrins are presently of interest to researchers [1] due to their capability of self-organizing through coordination of the pyridyl group of one molecule by the metal ion of a neighboring molecule. A great number of supramolecular sets has been obtained from the Zn, Ru, and Os metalloporphyrins. At the same time, the similar properties of Co and Fe porphyrinates, which are important due to their biological activity, remain poorly studied.

The specific nature of reversible oxygen coordination by sublimed layers of *meso*-tetrapyridyl-substituted Co porphyrins (CoT4PyP and CoT3PyP) was previously reported in [2–4]. In this case, the frequency $v(O_2)$ of the coordinated oxygen was about 100 cm⁻¹ lower, while the thermal stabilities of these complexes were noticeably higher, than that in oxygen coordination by sublimed layers of the tetraphenyl derivative CoTPP [5]. The differences observed were interpreted as the formation of oligomers in the solid phase of pyridyl-substituted derivatives as a result of coordination of the pyridyl group of one molecule by a cobalt atom of the nearest molecule.

It was recently discovered that the low-temperature sublimed layers of cobalt *meso*-mono-4-pyridyltriphenylporphyrinate (CoM4PyTPP) reversely bind oxygen in two different ways [6], i.e., with the formation of pentacoordinated complexes, such as CoTPP \cdot O₂ [5], and with the formation of hexacoordinated complexes with the pyridyl group in the *trans*-position to oxygen. Therefore, studies of the interaction of the simplest ligands with metal complexes of pyridylporphyrins make it possible to establish the structure of their sublimed layers, which is important to know for their use in optoelectronic devices.

This work deals with spectral studies of the interaction of carbon monoxide with sublimed layers of iron(II) *meso*-mono-4-pyridyltriphenylporpyrinate (FeM4PyTPP) (\mathbf{A}) compared to its structural analog FeTPP (\mathbf{B}), which is widely used in investigations.



Since Fe(II) porphyrinates are easily oxidized in air to form μ -oxodimers, in our work, we used a more stable hexacoordinated dipiperidine extracomplex, FeM4PyTPP(Pip)₂. H₂M4PyTPP was obtained by the mixed aldehyde method [7]. The compound purity was confirmed by data from thin-layer chromatography and NMR and UV spectroscopy, which coincided with the data cited in [7]. FeM4PyTPP(Pip)₂ and FeTPP(Pip)₂ were prepared as described in [8].

 $C^{18}O$ (enriched to 81.4%) was purchased from the Institute of Isotpes (Georgia).

ν	FeTPP · 2CO	FeM4PyTPP · 2CO	FeTPP · CO	FeM4PyTPP · CO	FeM4PyTPP*	FeM4PyTPP**
ν {CO(C ¹⁸ O)}	2032 (1982)	2031 (1981)	1964 (1918)	1985 (1940)		
I	1352	1352	1342	1350	1349	1343, 1350
II	795	796	803	795, 803sh	802	795, 802sh
III	462	462	436	463	467, 435svs	435, 467vs

Frequencies of coordinated CO and of the structurally sensitive vibrations (cm⁻¹) [11] in IR spectra of carbonyl FeTPP and FeM4PyTPP extracomplexes in their sublimed layers

* Freshly sublimed layer at 80 K.

** At T = 293 K, after carbonyl complex decomposition through evacuation at increased tamperature for many hours.

FeM4PyTPP(Pip)₂ (about 10 mg) was placed in a Knudsen cell and was kept under high vacuum (~10⁻⁵ torr) at $T \approx 250^{\circ}$ C for several hours. This procedure resulted in complete detachment of the axial ligands, which was varified by vacuum measurements at the cryostat outlet. Then, the cell temperature was raised to 300–350°C and sublimation of FeM4PyTPP was conducted for 2–3 h onto a CsI plate located in the optical cryostat and cooled with liquid nitrogen. CO (C¹⁸O) was thoroughly dried over P₂O₅ and supplied to the cryostat at a low rate from a vessel equipped with a manometer to measure the equilibrium pressure in the cryostat.

IR spectra were recorded on a Specord M-80 spectrophotometer. The spectral slit width was 4 cm⁻¹ when measuring outline spectra and 2 cm⁻¹ when taking spectra in the regions of structurally sensitive vibrations of iron porphyriantes (see below). The electronic absorption spectra were recorded on a Specord M-40 spectrophotometer, and NMR spectra were measured using Varian Mercury 300 spectrometer (solution in CDCl₃).

The low-temperature sublimed layers of metal complexes of *meso*-tetraarylporphyrins have a microporous structure [5] like that of their bulky samples [9]. Therefore, potential ligands can easily diffuse into the bulk layer. The obtained adducts can be characterized by spectral methods; solvent interference is absent in this case.

At liquid nitrogen temperature and at a CO equilibrium pressure of ~1 torr in the cryostat, the layers of the studied metalloporphyrins consist mainly of dicarbonyl complexes with a frequency of antiphase stretching vibiations of v_{as} {CO(C^{18} O)} at 2030(1980) cm⁻¹ [10]. The data in the table reveal that the frequencies v(CO)due to the dicarbonyl complexes of both metalloporphyrins are very close. At the same time, the frequencies and shapes of the bands of the monocarbonyl complexes are different. The singlet band v(CO) in the spectrum of the monocarbonyl complex FeTPP does not show significant frequency shifts with temperature growth; this is accompanied by decomposition of the thermally unstable dicarbonyl complex and by the formation of additional amounts of the monocarbonyl complex. In the case with FeM4PyTPP and at liquid nitrogen temperature, this band consists of two superposed bands (Fig. 1, spectrum a). When the layer is heated, the maximum of the combined band shifts upfield and v(CO) turns out to be ~20 cm⁻¹ higher than the respective band in the spectrum of the FeTPP · CO extracomplex (Fig. 1, spectra *b*, *c*).

The monocarbonyl complexes of the metalloporphyrins under consideration also greatly differ in thermal stability. In the case of FeM4PyTPP, evacuation at ~230 K results in complete decomposition of the dicarbonyl complex. The intensity of the monocarbonyl complex band (1985 cm⁻¹) increases. For CO detachment to be full, the evacuation should be conducted at 353 K for several hours. With FeTPP, evacuation performed at a lower temperature (~230 K) and resulting in decomposition of the dicarbonyl complex is accompanied by partial decomposition of the monocarbonyl compound with v(CO) at 1964 cm⁻¹. In this case, the coordinated CO is completely eliminated during evacuation over several dozens of minutes even at room temperature. The increased thermal stability of the monocarbonyl complex FeM4PyTPP agrees with data from [12] on the correlation between the stability of carbonyl complexes of iron porphyrinates and the frequency v(CO) of the extracomplex; i.e., more stable complexes exhibit higher values of v(CO).

The investigated porphyrins also behave in different ways when the layer heated to room temperature and containing monocarbonyl complexes is again cooled. With the same equilibrium pressures of CO in the cryostat, the concentration of a newly formed dicarbonyl complex is sufficiently higher in the case of FeTPP (Fig. 2, spectra a, b).

Distinctions discovered in the behavior of two metalloporphyrins with close structures can be explained if the coordination bond is suggested to form in the sublimed layer between the pyridyl group of one molecule and the iron ion of the neighbouring molecule in the case of the pyridyl-substituted derivative. With rapid freezing out of translational degrees of freedom of the molecules in the course of porphyrin sublimation onto a low-temperature surface, the concentration of such structures in the layer is small. The layer mainly consists of tetracoordinated FeM4PyTPP molecules capable of forming hexacoordinated dicarbonyl and pentacoordinated monocarbonyl complexes when CO is supplied. An increase in the temperature of the support is



Fig. 1. IR spectra of a sublimed FeM4PyTPP layer in the region of stretching vibrations of coordinated CO in the presence of CO (p = 1 torr) at (a) 80 K; (b) at ~230 K, after evacuation of the layer characterized by the spectrum a; and (c) at ~230 K, after short-time evacuation of the FeTPP layer containing carbonyl complexes.

accompanied not only by decomposition of the dicarbonyl complex but also by growth in the mobility of molecules in the layer, which results in the formation of hexacoordinated monocarbonyl complexes with a pyridyl group of the neighboring molecule in the sixth coordination position. When the layer is kept at increased but still low temperatures (below room temperature), the concentration of these extracomplexes with v(CO) = 1985 cm⁻¹ increases, while the concentration of pentacoordinated monocarbonyl complexes with v(CO) \approx 1964 cm⁻¹ decreases. In the UR spectrum,



Fig. 2. Regions of stretching vibration of the coordinated CO in IR spectra of sublimed layers of (*a*) FeM4PyTPP and (*b*) FeTPP in the presence of CO (p = 1 torr) after heating the low-temperature sublimate to room temperature and subsequent cooling to 80 K.

this appears as a gradual shift of the combined band toward high frequencies.

The spectral changes due to the formation of two types of monocarbonyl complexes are not as pronounced here as in the case of the above-mentioned CoM4PyTPP + O₂ system [6], since for the latter system, $\Delta v(O_2)$ in the penta- and hexacoordinated adduct with the additional pyridyl group in the fifth position amount to 80 cm⁻¹, whereas in the system under study, $\Delta v(CO) \approx 20$ cm⁻¹ and they do not split due to the large half-width of the bands.

The layer produced by FeM4PyTPP sublimation on the surface at room temperature and its subsequent exposure to an atmosphere of CO with further cooling to 77 K has v(CO) = 1985 cm⁻¹, while the band from the dicarbonyl complex can barely be distinguished in the spectrum. The same situation is observed in the case of low-temperature sublimates kept under vacuum for several days at room temperature. The most reasonable interpretation of these data is the formation of oligomeric structures in the layer with a low content of oligomer terminal molecules capable of forming dicarbonyl complexes.



The other possible reason for the observed differences between the monocarbonyl complexes FeTPP and FeM4PyTPP associated with the intramolecular effect of the pyridyl group on the electronic structure of Fe(II) and, thus, on the frequency of the coordinated CO cannot explain any of the listed experimental data. Moreover, this mechanism should also affect the frequency v_{as} (CO) of the dicarbonyl extracomplexes; this is not actually observed.

Unlike the CoTPP extracomplexes, in the case of FeTPP, the axial coordination has an effect on the vibrational spectrum of porphyrin itself [11, 13]. This occurs due to the close values of the energies of the d_{π} -orbitals of the metal and the π -orbitals of porphyrin in the Fe complexes. The interaction of the metal *d*-orbitals with the porphyrin π -orbitals, which is almost absent in the other transition-metal porphyrinates due to a great difference in the energies, leads, in the case of the Fe [11, 13] and Mn [14] porphyrinates, to a situation wherein the electronic effects caused by the axial coordination can directly influence the electronic density distribution in the macrocycle itself. As a result, certain standard vibrations of the macrocycle become sensitive to the nature of the extraligand and to the type of its coordination with the central metal ion.

As we expected, the IR spectra of FeM4PyTPP and FeTPP are very close. The main difference lies in the higher intensity of the band at 1600 cm⁻¹ in the FeM4PyTPP spectrum; this band in the spectra of the metal complexes of the *meso*-tetraphenylporphyrin is

assigned to vibrations with a predominate contribution v(CC) from the phenyl rings [15]. The pyridyl ring vibration with a similar shape also lies in this range, while the additional asymmetry produced by the nitrogen atom favors an increase in the intensity of the respective band. Identical IR spectra suggest that FeM4PyTPP will also exhibit the regularities we observed in the FeTPP extracomplexes.

A large number of IR spectra was examined in [11, 13] for penta- and hexacoordinated FeTPP complexes with N, O, S, and C donor ligands to reveal three bands (I-III) assigned to standard vibrations of the macrocycle, which are sensitive to the nature and number of axial ligands present. The positions of these bands in the spectrum of the monocarbonyl complex of FeM4PyTPP coincides with their positions in the spectra of hexacoordinated complexes but differs from the positions of the respective bands in the spectrum of the pentacoordinated FeTPP \cdot CO complex (table), which also supports the suggested mechanism. The structurally sensitive frequencies of FeM4PyTPPP itself, which was produced after decomposition of the carbonyl complex through evacuation at increased temperatures, are very close to the frequencies of pentacoordinated high-spin FeTPP complexes [2].

One more argument in favor of the main conclusion can be found when considering the band at 1600 cm⁻¹, which, in the case of FeM4PyTPP sublimed layers, unlike FeTPP layers, is sensitive to the availability of the axial ligand. The high-frequency region of this band



Fig. 3. IR spectra of a sublimed FeM4PyTPP layer in the region of v(CC) of the aryl rings after deposition at (*a*) 80 K, (*b*) after the layer is exposed to CO and heated to room temperature, and (*c*) after evacuation at 353 K over several hours.

in the spectrum of the monocarbonyl FeM4PyTPP complex contains a shoulder which disappears after removal of CO through evacuation at increased temperatures (Fig. 3, spectrum c). The shape of this band also differs from that of the band observed in the spectrum of the FeM4PyTPP layer sublimed on a low-temperature surface (Fig. 3, spectrum a).

As we said above, this band is due to the standard vibrations of the pyridyl ring. In the case of pyridine, it is a combined vibration involving v(CC) and β (CCH) [16], which is mostly shifted upfield in the course of coordination [17]. A similar situation is likely to occur in our case as well. An additional high-frequency shift of this band during coordination of CO in the sixth position should be explained in terms of its *trans*-effect,

which is significant due to the very strong π -acceptor properties of CO.

Thus, the conducted spectral measurements indicate that in the FeM4PyTPP sublimed layers, the oligomeric structures are realized due to intermolecular coordination bonds. As a result, the porosity of the layer with such structures should change. Molecules in the metal complexes of the *meso*-tetraphenylporphyrins are arranged in layers with the porphyrin rings located in parallel to one another. Pores in these compounds are long narrow channels lying opposite to the axial positions of the metals and are usually filled with solvent or ligand molecules. When these molecules are absent, the structure becomes substantially thicker and the cross section of the pores significantly decreases [9], preventing the reagents from diffusing into the bulk layer. This is the reason for the less effective coordination of CO by sublimed FeTPP layers kept under vacuum at room temperature for several days.

When the metalloporphyrin molecules contain functional substituents capable of specific intermolecular interactions (hydrogen bonds, coordination, etc.), the supramolecular organization of the system can noticeably change [18–20]. For 4-pyridyl-substituted derivatives, such coordination will evidently make the neighboring molecules orient themselves perpendicular to one another and will result in the formation of substantially larger pores [21] as compared to those formed in thickened MTPP structures. Indeed, the sublimed FeM4PyTPP layers also effectively bind CO when the layer is stored for several weeks. Moreover, this capability also appears when the layer is exposed to a mixture of atmospheric air and CO, with the content of the latter component being less than 1%. The spectral measurements show that, unlike FeTPP, the layers of FeM4PyTPP are oxidized very slowly (the appearance and growth in the intensity of the band v_{as} (Fe–O–Fe) of the μ -oxodimer in the range of 879 cm⁻¹) even when kept in air.

The discovered features of CO coordination by the sublimed FeM4PyTPP layers are expected to prove useful in practice.

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