IR Study of the Interaction of Dioxygen with [*meso*-Triphenyl(4-pyridyl)-porphyrinato]cobalt(II)

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The interaction of O_2 ($^{18}O_2$) with [*meso*-triphenyl(4-pyridyl)-porphyrinato]cobalt(II) [Co(MPyTPP)] has been investigated by means of IR spectroscopy under matrix-isolation conditions and by the action of dioxygen on thin sublimed layers. These studies have led to the characterisation of two dioxygen adducts: (1) a very unstable dioxygen adduct similar to that observed earlier for the closely related [*meso*-tetraphenylporphyrinato]cobalt(II) Co(TPP), and (2) a new type of coordinated O_2 ($^{18}O_2$) complex which is formed after warming Co(MPyTPP) either in pure oxygen matrices, or as sublimed layers in the presence of oxygen. The $\nu(O_2)$ vibration in this second species is more than 100 cm^{-1} lower than in the first, and the dioxygen adduct thus formed is thermally stable at 200 K. This adduct is identified as a six-coordinate dioxygen complex, with one coordination site occupied by the pyridyl group of an adjacent Co(MPyTPP) molecule. In the sublimed layers, the capacity for self-assembly of Co(MPyTPP) oligomers leads to the formation of microporous solids containing coordinatively unsaturated metal ions which have the ability to bind oxygen reversibly upon storage at ambient conditions.

Introduction

Some metalloporphyrins (MP) are known to be efficient oxygen carriers and have been studied for potential applications in the fields of artificial hemoglobin, oxygen-permselective membranes, catalytically active electrode coatings, selective O_2 adsorbents and sensors.[1−6] Co^{II} porphyrins attract special attention due to the reversible character of their O_2 binding,[7] and their thin films are promising in applications which depend on specific chemoresponsive properties of materials.[8]

In order to generate selective chemoresponsive materials, molecularly sized binding sites or pores must be created, and pyridylporphyrins have recently become a focus of attention due to their ability to form microporous self-assembling arrays.[9] Very interesting results in this area are now available for Zn, Ru and Os porphyrins. However, the potential for the self-assembly of biologically important Co, Fe and Mn pyridylporphyrins has surprisingly received very little attention. This may be due to the ease of oxidation and the ability to form five- and six-coordinate species, including dioxygen-bridged and μ-oxo structures.

The construction of microporous materials containing coordinatively unsaturated metal ions in their network promises to be an attractive tool for tailoring materials with useful chemoresponsive properties. As was shown earlier, low temperature sublimed layers of MTPP (M = metal dication; TPP = *meso*-tetraphenylporphyrinato dianion), which exhibit ligand-binding properties in the amorphous state lose this ability upon crystallization during storage at ambient conditions.[10] This occurs as a result of the dramatically decreased cross-section of the pores in the absence of solvated or ligand molecules in these solids.[11] In contrast, pyridylporphyrins are now widely explored as building blocks for constructing nanoporous materials.[12] In these studies the pyridyl groups of the porphyrins are usually coordinated to the metal centre of another complex.[9,13] It is reasonable, however, to expect that metallopyridylporphyrins containing metal ions capable of axial coordination can form self-assembled arrays, as was observed for Zn(MPyTPP) (MPyTPP = *meso*-monopyridyltriphenylporphyrinato dianion).[14,15] Lin[16] observed such self-assembly in the course of the hydrothermal synthesis of MTPyP (M = Co, Mn; TPyP = *meso*-tetrapyridylporphyrin) leading to unique metalloporphyrin hexamers with large cavities. In these assemblies, however, the metal ions

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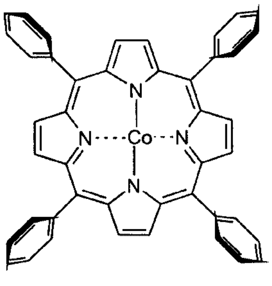
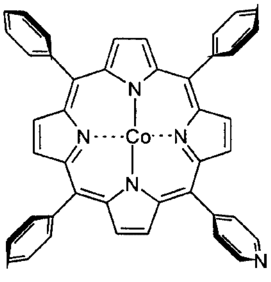
are coordinatively saturated. The same pattern was observed in sublimed films of CoT4PyP [T4PyP = *meso*-tetrakis(4-pyridyl)porphyrin][17] and CoT3PyP [T3PyP = *meso*-tetrakis(3-pyridyl)porphyrin],[18] which, although porous, slowly lose their O_2-binding ability due to the formation of coordinatively saturated structures. It could be expected that in the metal-*meso*-pyridyltriphenylporphyrin compounds, in which the number of metal ions and pyridyl groups is equal, the probability of formation of six-coordinate saturated structures might be diminished.



A



B

In this paper the interaction of Co(MPyTPP) (**B**) with O_2 is studied under matrix isolation and solid-state conditions, and it is shown that this interaction differs significantly from that of the closely related Co(TPP) (**A**).

Results and Discussion

As expected from the closely related structures, the IR spectrum of Co(MPyTPP) (Figure 1a) in an Ar matrix is very similar to that of Co(TPP) reported elsewhere.[19] Isolation of this compound in a pure oxygen matrix ($^{16}O_2$) leads to the immediate appearance of a new band at 1286 cm^{-1} (Figure 1b), which has a counterpart at ca. 1208 cm^{-1} when $^{18}O_2$ is used (Figure 1c). From the value of this isotopic shift, and by analogy with previous work,[19] these bands are readily assigned to coordinated dioxygen in the adducts Co(MPyTPP)($^{16}O_2$) and Co(MPyTPP)($^{18}O_2$).

It is interesting to note that experiments using pure oxygen matrices showed clear evidence of the intramolecular O-O stretching mode [ca. 1551 ($^{16}O_2$) and 1460 cm^{-1} ($^{18}O_2$)]. This stretching mode is technically forbidden in IR spectra and appears only very weakly in deposits of pure solid oxygen. Its apparent enhancement here may be connected with a possible interaction of the O_2 molecule with the π-cloud of the porphyrin macrocycle or with the coordinated dioxygen adduct. The latter interpretation seems to be more probable, in view of the polar nature of coordinated O_2 and of the high sensitivity of its stretching band to the environment. For example, in our experiments the $\nu(O_2)$ of coordinated dioxygen was observed at 1286, 1279 and 1251 cm^{-1} in an O_2 matrix, an Ar matrix and in the sublimed layer, respectively.

In contrast to previous studies on Co(TPP), slow warming of matrix-isolated samples up to 200 K results in disappearance of the 1286 cm^{-1} band, indicating decomposition of this species, and the appearance of a new band at about 1170 cm^{-1} (Figure 2a) in the same spectral region where a triad of porphyrin bands may be found in the solid state (Figure 4a). The same procedure with isotopically enriched $^{18}O_2$ samples leads to the appearance of a new band at 1103 cm^{-1} (Figure 22b). This isotopic dependence confirms its assignment as a dioxygen stretching mode, and indicates the formation of another type of complex.

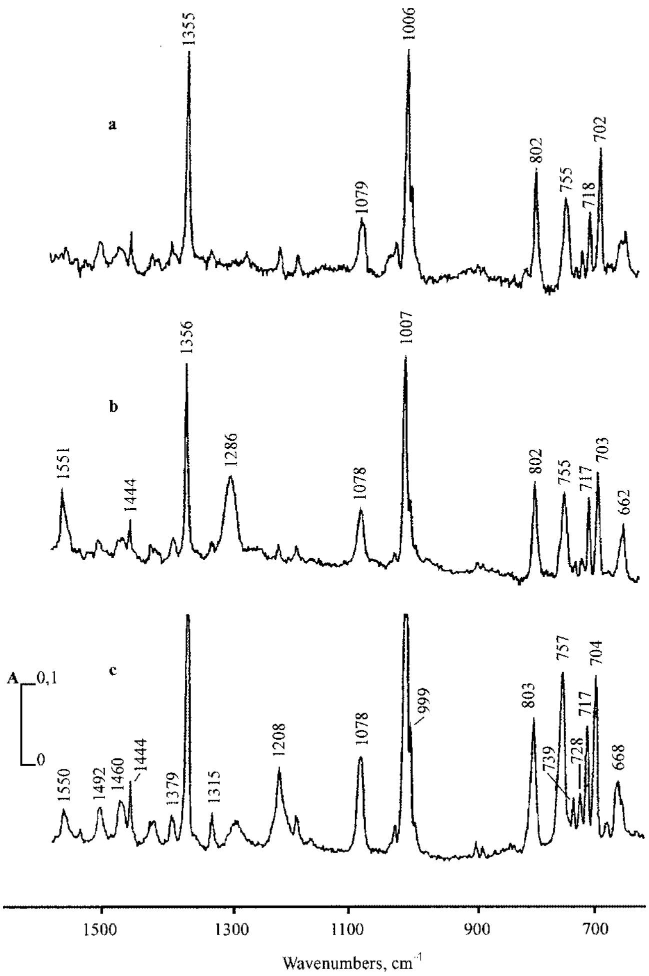


Figure 1. IR spectra of Co(MPyTPP) isolated in Ar (a), $^{16}O_2$ (b), and $^{18}O_2/^{16}O_2$ = 7/3 (c) matrices at 12 K

We believe that this band should be assigned to the six-coordinate dioxygen complex in which one coordination site is occupied by the pyridyl group of an adjacent Co(MPyTPP) molecule. In this process, the slow warming of the dioxygen matrix results in the slow elimination of free O_2, and the formation of coordination links with adjacent molecules to form the six-coordinate dioxygen complex represented in Figure 3.

It is to be anticipated that this type of coordination involving a base ligand in an axial position (*trans* to dioxygen) would shift $\nu(O_2)$ to markedly lower frequency, while the $\nu(Co-O_2)$ band should shift upward. Such a ligand would increase the amount of electron donation to the metal d orbitals, thus enhancing the $M-O_2$ bond strength (and hence the thermal stability of the complex) but would consequently weaken the O−O bond by increasing the net

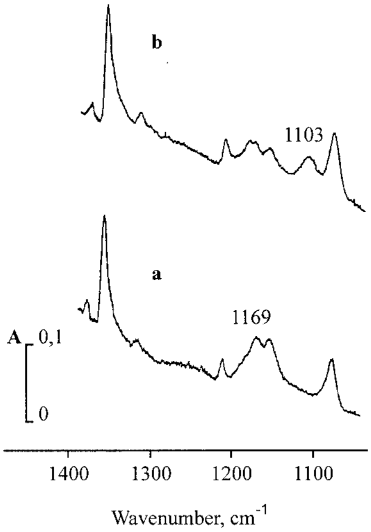


Figure 2. IR spectra of Co(MPyTPP) initially isolated in $^{16}O_2$ matrix at 12 K, warmed to 200 K and recooled (a); (b) the same as (a) with an isotopic mixture $^{18}O_2$/$^{16}O_2$ of 7/3

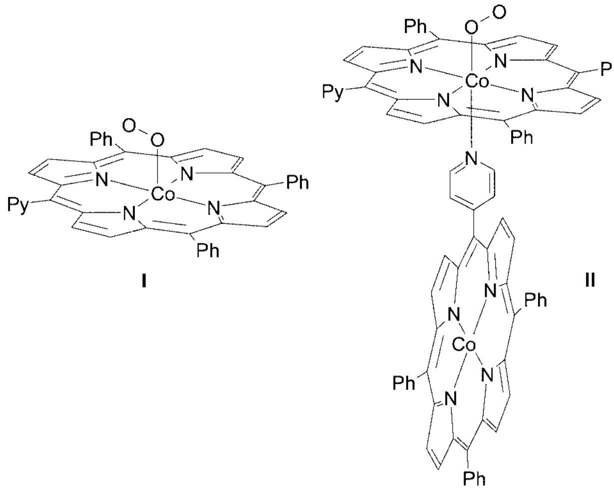


Figure 3. Schematic view of dioxygen complexes of Co(MPyTPP) produced in an O_2 matrix (I) and after elimination of O_2 by warming of sample to 200 K (II)

occupancy of the antibonding $\pi_g^*(O_2)$ orbitals. This effect has been quantitatively demonstrated by Nakamoto and co-workers for a series of Co(TPP)(base)(O_2) complexes, where the $\nu(O_2)$ frequency decreases linearly as the pK_a of the base increases.[20] It is also worth noting that in the Raman spectra of the six-coordinate (O_2)Co(TPP)(B) complexes (where B is a nitrogen base), the $\nu(O_2)$ bands are observed in the vicinity of 1160 cm^{-1}.[20]

The ability of Co-*meso*-aryl-substituted porphyrins to bind dioxygen is inherent not only for the isolated molecules (i.e. matrix-isolated or solvated molecules) but is also found in the layers obtained by sublimation onto a low-temperature (77 K) substrate. These layers are both amorphous and microporous,[10] with the result that interacting gases can easily diffuse into the bulk of the layers. The adducts thus formed can be studied by IR spectroscopy without solvent interference.

A study of thin layers of Co(MPyTPP) obtained by sublimation onto a support cooled with liquid nitrogen in the presence of 60 Torr O_2 reveals two new IR bands at 1251 and 1167 cm^{-1} (Figure 4b). After the support is 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 expense of the high frequency band.

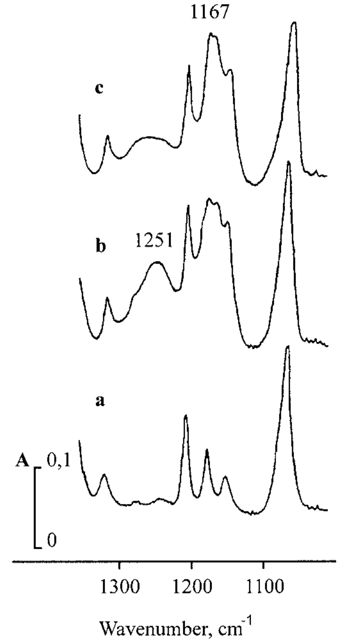


Figure 4. IR spectra of CoMPyTPP sublimed layer at 80 K (a), after exposure to 60 Torr O_2 and annealing in the cycle 80 K → 120 K → 80 K (b); (c): the same as (b) with the layer obtained by sublimation onto a room temperature substrate

When oxygen gas is admitted to layer samples prepared at 77 K and stored for one day at room temperature, the IR spectrum again shows a relatively weak band at 1251 cm^{-1}, with the band at 1167 cm^{-1} substantially increased in intensity. The same pattern is observed for the layers obtained by sublimation onto a room-temperature substrate (Figure4c).

These results can be interpreted as follows. In the related Co(TPP) system, the reversible nature of dioxygen binding by sublimed layers has been shown previously,[10] and the band at 1250 cm^{-1} has been attributed to $\nu(O_2)$ of the Co(TPP)(O_2) adduct, with the assignment confirmed by experiments with $^{18}O_2$. In similar experiments with the *meso*-tetrapyridyl-substituted derivatives CoT4PyP[17] and CoT3PyP[18] the $\nu(O_2)$ bands of bound dioxygen appear in the 1160 cm^{-1} region (ca. 1100 cm^{-1} for $^{18}O_2$) and the adducts obtained are thermally much more stable than those produced with Co(TPP). These differences were explained in terms of formation of coordinatively linked polymers and formation of a six-coordinate dioxygen adduct with the pyridyl base in the *trans* axial position.

In this work there is additional spectral evidence of such coordination links in Co-pyridyl porphyrins. The single medium-intensity band of Co(TPP) at ca. 1600 cm^{-1}, which corresponds to the C=C stretching of the phenyl groups in Co(MPyTPP) gains intensity, and becomes complex due to mixing with the C=N stretching of the pyridyl group. This band exhibits well-defined changes upon annealing of the layer (Figure 5). The high frequency shoulder in the low temperature sublimate gains intensity after annealing and, as a result, the peak maximum shifts to higher wavenumbers (by about 8 cm^{-1}). This observation is consistent with the increasing number of coordinated pyridyl groups, since it is known[21] that coordination of pyridine to metal ions leads to a high frequency shift of this mode. The same spectral pattern represented in the upper spectrum of Figure 6 is observed when a sublimed layer is formed by deposition onto a room-temperature substrate.

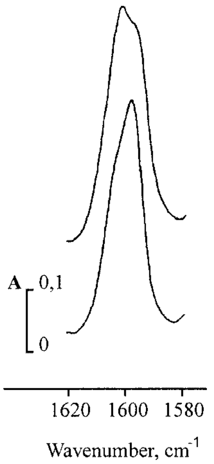


Figure 5. IR spectra of Co(MPyTPP) sublimed layer in the region of the skeletal vibrations of aryl substituents at 80 K: after deposition onto a low temperature substrate (lower curve); after warming to room temperature and recooling (upper curve)

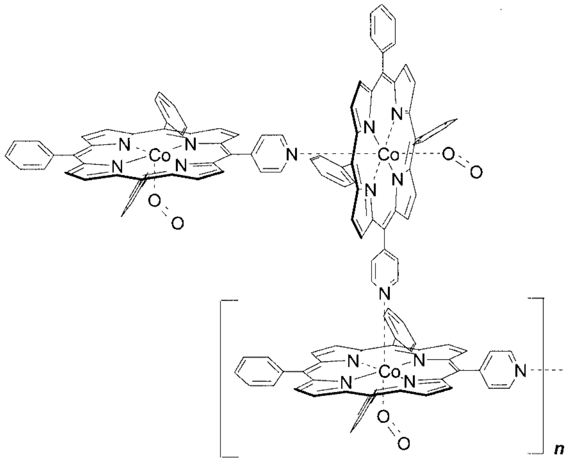


Figure 6. Schematic view of a coordination oligomer produced in sublimed layers of Co(MPyTPP) and its dioxygen adducts

On the basis of these results it can therefore be concluded that both the warming of a low-temperature Co(MPyTPP) sublimed layer and the deposition of Co(MPyTPP) onto a room-temperature substrate lead to the formation of one-dimensional coordination oligomers as represented in Figure 6. This same structure has been observed for $[Zn(MPyTPP)]_n$, for which X-ray analysis established that the pyridyl group of the porphyrin periphery is bound to the metal centre of an adjacent porphyrin, thereby creating a polymer with a long chain and a zigzag conformation.[14,15]

As a result of their low-temperature O_2-binding ability, sublimed layers of Co(MPyTPP) may therefore offer major advantages over the previously investigated systems Co(TPP), Co(T4PyP) and Co(T3PyPP). As mentioned above sublimed layers of Co(TPP) lose their O_2-binding ability upon storage at room temperature. Co(T4PyP) and Co(T3PyP) layers stored in vacuo for a week under the same experimental conditions bind only 50% of the initial quantities. In contrast, the amount of bound dioxygen in Co(MPyTPP) layers stored at room temperature for one month decreases by less than 20%, based on the decreased intensity of the 1167 cm^{-1} $\nu(O_2)$ band. It worth noting that this capability for low-temperature O_2-binding is also retained for the layers stored in air. Apparently the zigzag conformation of oligomer chain prevents the formation of dioxygen-bridged structures, which leads to the irreversible oxidation of the metal ions.

Conclusions

[*meso*-Triphenyl(4-pyridyl)porphyrinato]cobalt(II) Co(MPyTPP) binds dioxygen both under matrix isolation conditions and in the solid state. The self assembly of Co(MPyTPP) in sublimed layers lead to the formation of one-dimensional coordination oligomers containing coordinatively unsaturated Co^{II} in its chains. Similar to other pyridyl-porphyrin arrays the layers have a microporous structure and their low-temperature O_2-binding ability is conserved on storing in air.

The areas in which this property can be used are now the primary focus of our attention. Preliminary data indicate, for instance, that sublimed layers of CoMPyTPP can selectively bind dioxygen from CO/O_2 mixtures and can therefore serve as a device for the purification of CO by removing trace quantities of O_2.

Experimental Section

Co(MPyTPP) was obtained from H_2MPyTPP, which was synthesised according to a previously reported procedure.[22] NMR and UV/Vis spectra were in good agreement with reported data.[22] In a typical experiment, Co(MPyTPP) was placed in a Knudsen cell and was first heated to about 400 K under high vacuum ($P < 10^{-6}$ Torr) to remove solvent molecules.[11] The CsI substrate of the optical cryostat was then cooled to ca. 12 K using a closed-cycle Displex refrigeration system. The matrix-isolation apparatus and general methodology used have been described elsewhere.[23] Co(MPyTPP) was sublimed at ca. 520 K together with a large excess of Ar (BOC, 99.999%), Ar/O_2, or pure O_2 (BOC, 99, 999%). O-18 enriched samples were obtained using a mixture of $^{18}O_2$ + $^{16}O_2$ in the mol ratio 7:3, as established by mass spectrometry.

The interaction of O_2 with sublimed layers of Co(MPyTPP) was carried out in the optical cryostat, such that the deposited film was obtained by sublimation on the low (77 K) or room-temperature substrate according to published procedures.[10] In a typical procedure, thoroughly dried and pre-cooled oxygen was slowly fed into the cryostat from a vessel attached to a mercury gauge for measurements of O_2 pressure. The sublimed layer was then stored for 30 min while the temperature was alternated in the following sequence: 80 → 120 → 80 K. The oxygen gas was then pumped off and IR spectra obtained over a range of temperatures.

Infrared spectra were recorded using Perkin−Elmer PE983G and Specord M-80 instruments, linked to appropriate data-handling systems. UV/Visible spectra were obtained on a Specord M-40 spectrophotometer, and $CDCl_3$ − solution NMR spectra were obtained on a Varian Mercury instrument.

Acknowledgments

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