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### STERIC HINDRANCE INFLUENCE OF IRON(II)-PORPHYRINS ON O<sub>2</sub> AND CO BINDINGS: INFRARED AND RESONANCE RAMAN STUDIES

In designing model compounds for the active site of oxygen carrier hemoproteins, it is important to know the influence of steric hindrance on the O<sub>2</sub> and CO bindings. Indeed if in natural compounds the CO moiety adopt an end-on bent or tilted geometry from the perpendicular to the porphyrin plane [1], in various model complexes CO has been found to adopt a linear geometry [2]. This difference is attributed to distal group steric effect in the formers. On the contrary in both systems the Fe-O-O is bent [3-4].

As part of our studies of stereochemical influence on the formation and reactivity of carbonylated and oxygenated model compounds, we have prepared a new series of porphyrin derivatives specifically designed to investigate such a distal steric effect. The first observations of their infrared (IR) and resonance Raman (RR) spectroscopic studies are reported here.

All the single-face hindered porphyrins are derived from 5,10,15,20 tetraphenylporphyrin. The efficient protection of CO and O<sub>2</sub> coordination site is provided by a polymethylene chain anchored through amide linkage in *ortho* position of two *meso* phenyl groups in a cross configuration. The two other *meso* phenyl groups are substituted in

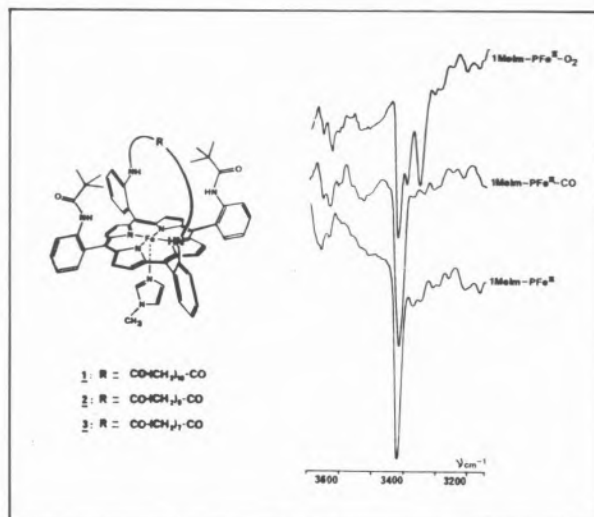


Fig. 1

IR NH stretching of compound 3

*ortho* position by a pivalamido residue. The presence of these "pickets" inhibits the sideways displacement of the anchoring "handle" in comparison with symmetrical "basket handle" porphyrins previously developed in our laboratory [5], as shown by the strong up-field shifts of methylene protons in <sup>1</sup>H NMR spectra of four-coordinated iron(II) derivatives which are affected by pseudo-contact interaction [6].

IR spectra of iron(II) CO and O<sub>2</sub> complexes were recorded on a Nicolet 5MX FT/IR spectrometer at 4 cm<sup>-1</sup> resolution. All RR spectra were obtained with excitation at 441,6 nm using a He/Cd laser (Liconix, model 4050). Samples were prepared by bubbling (1 atm) <sup>12</sup>CO, <sup>13</sup>CO (CEA, France, 99 atome %), <sup>16</sup>O<sub>2</sub> and <sup>18</sup>O<sub>2</sub> (CEA, France, 98 atome %) in a toluene or benzene solution of iron(II) derivatives (10<sup>-4</sup> M) and *N*-methylimidazole (10<sup>-2</sup> M). IR spectra of carbonylated derivatives reveal a gradual shift of <sup>12</sup>C-O stretching vibrations from 1960 cm<sup>-1</sup> (1) to 1948 cm<sup>-1</sup> (3) which are very different from the observed frequency at 1970 cm<sup>-1</sup> of unhindered ferrous-porphyrins CO [7]. It should be noted that compound 3 exhibits ν<sub>CO</sub> not significantly different from those observed for carboxyhemoglobin and carboxymyoglobin [8]. RR spectra of <sup>12</sup>CO-1 and <sup>12</sup>CO-3 show a specific band at 488 cm<sup>-1</sup> and 506 cm<sup>-1</sup> respectively corresponding to the Fe-<sup>12</sup>CO stretching mode. These bands are sensitive to <sup>13</sup>CO isotopic substitution and are shifted to 484 and 501 cm<sup>-1</sup>. The decrease in the C=O stretching frequencies as well as the

increase in the Fe-CO stretching frequencies may be caused by a tilted or bent configuration of the carbonyl compounds due to increasing steric hindrance. This is in agreement with previous results obtained by YU *et al.* [9].

RR and IR spectra of oxy derivatives have also been recorded. RR bands at 562 and 559  $\text{cm}^{-1}$  in the spectra of  $^{16}\text{O}_2$ -1 and  $^{16}\text{O}_2$ -3 are shifted by 23  $\text{cm}^{-1}$  to the low frequency region upon substitution by  $^{18}\text{O}_2$  and clearly arise from the Fe-O<sub>2</sub> stretching modes. The Fe-O<sub>2</sub> frequency was observed at 568  $\text{cm}^{-1}$  for  $^{16}\text{O}_2$ -iron(II) "picket fence" porphyrin [10]. The significant difference of 6  $\text{cm}^{-1}$  between our less hindered compound 1 and Collman's model can be attributed both to the steric effect and the hydrogen bond between the oxygen atom not liganded to the iron and the NH group of one of the "handle" amides in 1 [11]. The comparison of IR spectra of 1, 2 and 3 and their O<sub>2</sub> and CO adducts gives further evidence for the latter interaction. All show the presence of one intense band at 3422-3425  $\text{cm}^{-1}$  due to amide NH-stretching vibration (Fig. 1). An additional weaker band is observed only with oxygenated complexes in the 3372-3355  $\text{cm}^{-1}$  range. The intrinsic shift induced by the presence of the oxygen molecule for the NH stretch is thus larger than 50  $\text{cm}^{-1}$  and is consistent with an intramolecular hydrogen bond formation. However, the balance between these frequencies may depend upon a change in O<sub>2</sub> configuration due to steric hindrance within the coordination cavity.

Studies with the aim of correlating spectral properties of these compounds with their O<sub>2</sub> and CO affinities are now in progress in this laboratory.

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## REVERSIBLE OXIDATION OF IRON(II) N-METHYLPORPHYRINS. CHARACTERIZATION OF THERMALLY UNSTABLE IRON(III) N-METHYLPORPHYRINS

Oxidation of  $\text{NCH}_3\text{TPPFeX}$  and  $\text{NCH}_3\text{OEPFeX}$  ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ;  $\text{NCH}_3\text{TPP}$  is anion of *N*-methyl-tetraphenylporphyrin,  $\text{NCH}_3\text{OEP}$  is anion of *N*-methyloctaethylporphyrin) yields the Fe(III) complexes of the respective *N*-methylporphyrin (*i.e.*  $[\text{NCH}_3\text{TPPFeX}]\text{X}'$  1 and  $[\text{NCH}_3\text{OEPFeX}]\text{X}'$  2). The following oxidizing agents have been used:  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ . The oxidation is reversible. The oxidation product is thermally unstable and decomposes to several compounds depending on the X ligand.  $\text{TPPFeX}$ ,  $\text{CH}_3\text{X}$ ,  $\text{NCH}_3\text{TPPH}$ , Fe(III) and a  $\mu$ -oxo dimer have been identified.