

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 cm^{-1} in the spectra of $^{16}\text{O}_2$ -1 and $^{16}\text{O}_2$ -3 are shifted by 23 cm^{-1} to the low frequency region upon substitution by $^{18}\text{O}_2$ and clearly arise from the Fe-O₂ stretching modes. The Fe-O₂ frequency was observed at 568 cm^{-1} for $^{16}\text{O}_2$ -iron(II) "picket fence" porphyrin [10]. The significant difference of 6 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 O₂ and CO adducts gives further evidence for the latter interaction. All show the presence of one intense band at 3422-3425 cm^{-1} due to amide NH-stretching vibration (Fig. 1). An additional weaker band is observed only with oxygenated complexes in the 3372-3355 cm^{-1} range. The intrinsic shift induced by the presence of the oxygen molecule for the NH stretch is thus larger than 50 cm^{-1} and is consistent with an intramolecular hydrogen bond formation. However, the balance between these frequencies may depend upon a change in O₂ configuration due to steric hindrance within the coordination cavity.

Studies with the aim of correlating spectral properties of these compounds with their O₂ and CO affinities are now in progress in this laboratory.

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PS4.9 — TH

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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 $\text{NCH}_3\text{OEPFeX}$ ($\text{X} = \text{Cl}^-$, Br^- , I^- ; NCH_3TPP is anion of *N*-methyl-tetraphenylporphyrin, NCH_3OEP 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: Cl_2 , Br_2 , I_2 . The oxidation is reversible. The oxidation product is thermally unstable and decomposes to several compounds depending on the X ligand. TPPFeX , CH_3X , NCH_3TPPH , Fe(III) and a μ -oxo dimer have been identified.

Complexes **1** and **2** have been characterized on the basis of ^1H NMR, ^2H NMR, ESR spectroscopies and electronic spectra.

The proton NMR resonances of **1** and **2** have been assigned by means of specific deuteration, intensity and linewidth analysis.

The *N*-methyl resonance appears at 285 ppm (-60°C , CDCl_3) and could be observed only by ^2H NMR on deuterium labeled samples.

Four pyrrole resonances of **1** and eight methylene resonances of **2** confirm a C_s symmetry imposed by *N*-methylation. The characteristic downfield resonance positions of pyrroles (133.2, 95.8, 79.5 ppm; -60°C) and ESR parameters ($g_\perp^{\text{eff}} = 5.9$, $g_\parallel^{\text{eff}} = 2.1$) prove that the oxidation has taken place on the iron. The ^6A ground state has been proposed.

The electron exchange between Fe(II) and Fe(III) complexes has not been observed.

The results of the paper should be relevant to the explanation of the green pigment formation in the course of cytochrome P-450 inactivation.



PS4.10 — MO

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MÖSSBAUER STUDY OF OXY-MODELS FOR THE ENZYME P450.

I: $[\text{Fe}(\text{O}_2)(\text{SC}_6\text{HF}_4)\text{TP}_{\text{PIV}}\text{P}][\text{Nac18C6}]$;

II: $[\text{Fe}(\text{O}_2)(\text{SC}_6\text{HF}_4)\text{TP}_{\text{PIV}}\text{P}][\text{Kc222}]$;

AND III: $[\text{Fe}(\text{O}_2)(\text{SC}_6\text{HF}_4)\text{TP}_{\text{PIV}}\text{P}][\text{Nac222}]$

Mössbauer data have been recorded in the temperature range between 4.2 K and 295 K, with and without externally applied magnetic field. Quadrupole splittings ΔE_Q have been plotted *versus* temperature in Fig. 1 to visualize the different tempe-

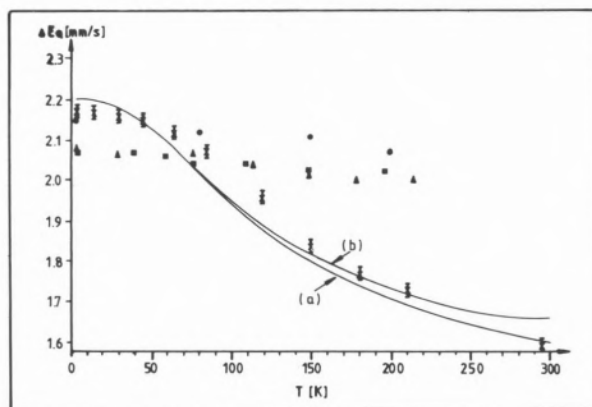


Fig. 1

Temperature dependent experimental quadrupole splittings for compounds **I** (X), **II** (■), **III** (▲), and P450 O_2 (●). The values for P450- O_2 are taken from M. SHARROCK et al. [4]. The solid lines correspond to (a) $V_{xx}^* = -0.95$, $V_{zz} = 1$, and (b) $V_{xx}^* = -0.95$, $V_{zz} = 1.5$ in eq. (1)