

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

R. MONTIEL-MONTOYA

E. BILL

A.X. TRAUTWEIN

H. WINKLER

Physik

Medizinische Hochschule

2400 Lübeck 1

W. Germany

L. RICARD

M. SCHAPPACHER

R. WEISS

Cristallochimie

Université Louis Pasteur

67070 Strasbourg

France

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-

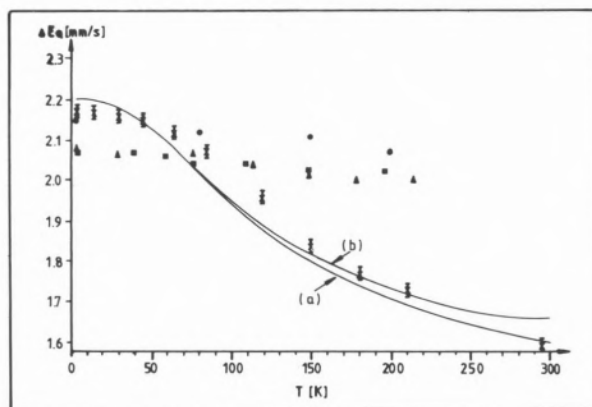


Fig. 1

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)

perature dependences. From a computer simulation of magnetic spectra the sign of the main component of the electric field gradient tensor (efg) V_{zz} turns out to be negative for **I** and **II**, and the asymmetry parameter η takes the values $\eta \sim 0$ at 4.2 K and $\eta \sim 0.5$ at 173 K for **I**, and $\eta \sim 0.3$ at 4.2 K for **II**.

Our interpretation of the pronounced temperature dependence in ΔE_Q of **I** is based on the three-di-

um amount of free parameters when we choose V_{zz} parallel to V_{xx}^* . Thus the efg tensor of 02A

$$\text{becomes } \begin{pmatrix} -2.2 & 0 & 0 \\ & 1.1 & 0 \\ & & 1.1 \end{pmatrix}$$

The overall efg tensor for the situation that 02B and 02C become Boltzmann-populated with temperature (and assuming fast relaxation among the three sites) is then given by:

$$V_{pq} = \left[\begin{pmatrix} -2.2 & 0 & 0 \\ & 1.1 & 0 \\ & & 1.1 \end{pmatrix} + 2 \begin{pmatrix} V_{xx}^* & 0 & 0 \\ & -V_{xx}^* & V_{zz} \\ & & V_{zz} \end{pmatrix} \exp(-190/kT) \right] / [1 + 2\exp(-190/kT)]. \quad (1)$$

mensional structure of this material, as derived from X-ray studies (Fig. 2). The occupation of sites 02A, 02B, and 02C at -100°C turned out to be approximately 0.5, 0.25, and 0.25, respectively.

From these numbers we estimate the energy barrier Δ which separates 02A from 02B and 02C: $\Delta \sim 190$ K. We now employ the assumption that sites 02B and 02C are equivalent, i.e. their efg tensors differ only by interchanging signs within elements V_{xz} and V_{yz} . Adding the two tensors thus

yields $2 \begin{pmatrix} V_{xx} & V_{xy} & 0 \\ & V_{yy} & 0 \\ & & V_{zz} \end{pmatrix}$. Appropriate rotation

about the z-axis (which we choose parallel to the heme-normal) finally yields $\begin{pmatrix} V_{xx}^* & 0 & 0 \\ & V_{yy}^* & 0 \\ & & V_{zz} \end{pmatrix}$.

The efg tensor of 02A is the only contribution to ΔE_Q at 4.2 K. In agreement with the findings of SPARTALIAN *et al.* [1] from their study of a similar model compound, with the findings from our single crystal study of MbO_2 [2], and with the results obtained from molecular orbital calculations [3], we choose V_{zz} such that it lies in the heme plane (x-y-plane). After testing several orientations for V_{zz} within this plane, we find the best possible fit of our experimental data for a mini-

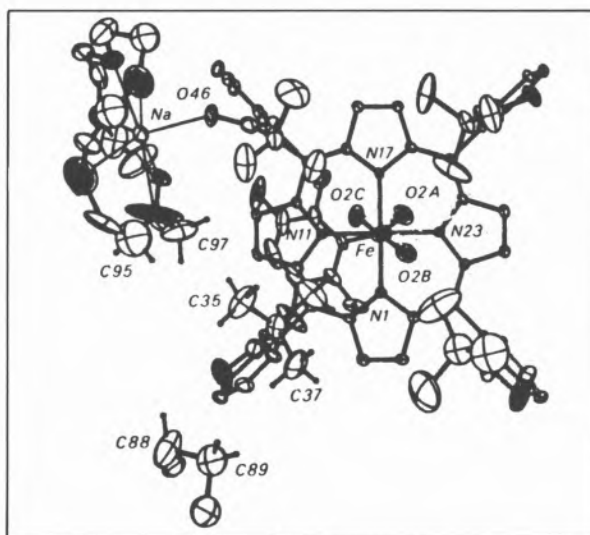


Fig. 2

ORTEP-plots for **I** obtained from X-ray studies at -100°C

All V_{pq} -values in eq. (1) are given in mms^{-1} .

Eq. (1) with the remaining parameters V_{xx}^* and V_{zz} explains the decrease of ΔE_Q and the increase of η with increasing temperature, and additionally the negative sign of V_{zz} at 4.2 K as well as at 173 K (curves a and b in Fig. 1).

Compound **II** shows only negligible temperature dependence in ΔE_Q . This is directly obvious from comparing the efg tensors of 02A and 02B of compound **II** (Fig. 3), which, under approximately C_2 -operation, result from each other. The overall efg tensor would then be:

$$V_{pq} = \left[\begin{pmatrix} V_{xx} & V_{xy} & V_{xz} \\ & V_{yy} & V_{yz} \\ & & V_{zz} \end{pmatrix} + \begin{pmatrix} V_{xx} & V_{xy} & -V_{xz} \\ & V_{yy} & -V_{yz} \\ & & V_{zz} \end{pmatrix} \exp(-\Delta/kT) \right] / [1 + \exp(-\Delta/kT)]. \quad (2)$$

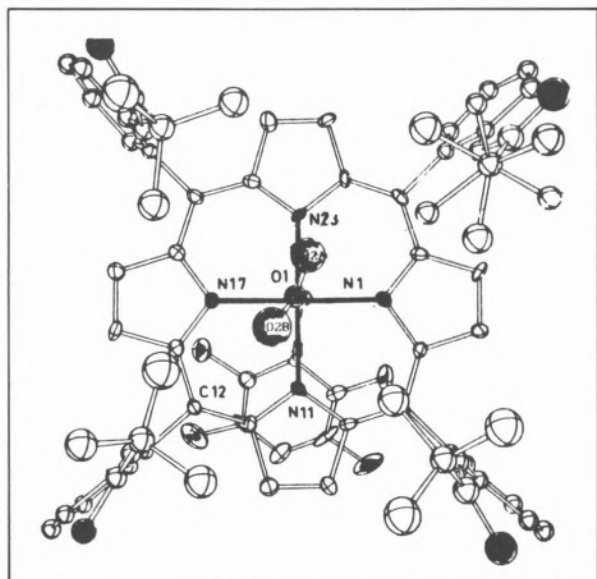


Fig. 3

ORTEP-plot for II obtained from X-ray studies at room temperature

From eq. (2) it is clear that in this case the temperature has only a minor influence in V_{pq} and hence in ΔE_Q .

REFERENCES

- [1] K. SPARTALIAN, G. LANG, J.P. COLLMAN, R.R. GAGNE, CH.A. REED, *J. Am. Chem. Soc.*, **63**, 5375 (1975).
- [2] Y. MAEDA, T. HARAMI, Y. MORITA, A.X. TRAUTWEIN, U. GONSER, *J. Chem. Phys.*, **75**, 36 (1981).
- [3] A.X. TRAUTWEIN, unpublished results.
- [4] M. SHARROCK, P.G. DEBRUNNER, C. SCHULZ, J.D. LIPSCOMB, V. MARSHALL, I.C. GUNSALUS, *Biochim. Biophys. Acta*, **420**, 8 (1976).



PS4.11 — MO

E. BILL

A.X. TRAUTWEIN

Physik

Medizinische Hochschule

2400 Lübeck 1

W. Germany

K. FISCHER

K.H. PAULI

Kristallographie

Universität des Saarlandes

6600 Saarbrücken 11

W. Germany

N. BLAES

U. GONSER

R. PRESTON

Angewandte Physik

Universität des Saarlandes

6600 Saarbrücken 11

W. Germany

F. SEEL

R. STAAB

Anorganische Chemie

Universität des Saarlandes

6600 Saarbrücken 11

W. Germany

LOW TEMPERATURE MOLECULAR DYNAMICS OF $[\text{HFe}(\text{CO})_4]^-$:

A POSSIBLE MODEL FOR THE DYNAMIC BEHAVIOR OF O_2 IN IRON-PORPHYRINS

Recently we have described the structure of compounds which have been synthesized from pentacarbonyl iron and *N*-substituted imidazole groups [1]. One of these compounds contains as cation hexa (1-ethylimidazole) iron(II) and as anion hydrido tetracarbonylferrate (-I), for which we use the shorthand notations $[\text{FeIm}_6]^{2+}$ and $[\text{HFe}(\text{CO})_4]^-$. In Fig. 1 we show the experimental Mössbauer spectra obtained at 288.7 K and 4.2 K. From the computer fits of these spectra using Lorentzian lines we derived isomer shifts and quadrupole splittings which are typical for high-spin ($S=2$) iron (curve 1) corresponding to $[\text{FeIm}_6]^{2+}$, and low-spin iron (curve 2) corresponding to $[\text{HFe}(\text{CO})_4]^-$. The zero quadrupole splitting at