

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  $\Delta E_Q$ .

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## LOW TEMPERATURE MOLECULAR DYNAMICS OF $[\text{HFe}(\text{CO})_4]^-$ : A POSSIBLE MODEL FOR THE DYNAMIC BEHAVIOR OF $\text{O}_2$ 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

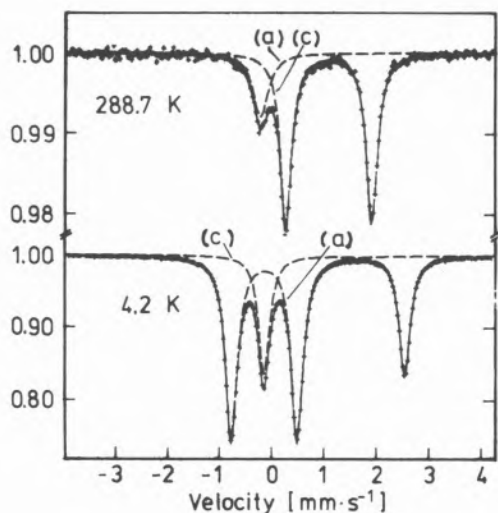


Fig. 1

Mössbauer spectra of the cation iron (curve 1) and anion iron (curve 2)

288.7 K may be due either to exact static tetrahedral (T) point-symmetry for the iron site in the anion, or due to dynamic effects. Decreasing the sample temperature from 288.7 K to 4.2 K has dramatic influence on the point-symmetry within the anion. At about 210 K the compound undergoes a reversible transition which increases the quadrupole splitting of the anion iron from zero to about 1.35  $\text{mm s}^{-1}$  within a temperature range of 30 K (Fig. 2), while the cation iron shows a temperature dependence of  $\Delta E_Q$  without abrupt changes, but characteristic for hexacoordinated high-spin ( $S=2$ ) iron [2].

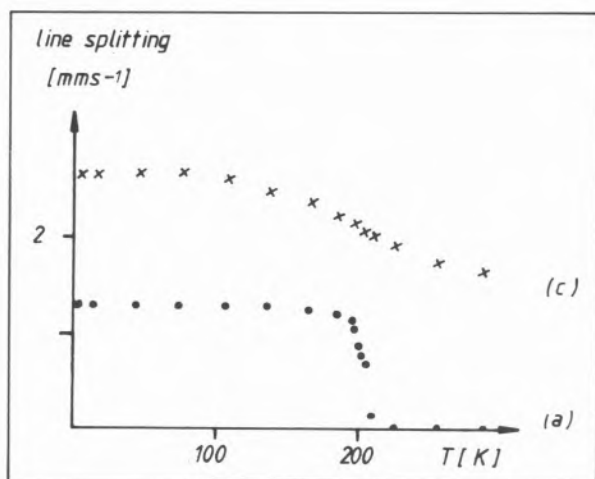


Fig. 2

Temperature dependence of experimental quadrupole splittings of the cation iron (x) and the anion iron (•), respectively

The peculiar temperature behavior of  $\Delta E_Q^{\text{anio}}$  indicates that we are concerned with dynamic effects rather than static tetrahedral point-symmetry of the iron site in the anion above 200 K.

Comparing the resonance absorption of cation iron (area  $A_1$  under curve 1 of Fig. 1) and anion iron (area  $A_2$  under curve 2 of Fig. 1) indicates that  $A_1:A_2$  is 4.35:1 at 288.7 K, in strong contradiction to the crystallographic result that the ratio  $\text{Fe}(\text{cation}):\text{Fe}(\text{anion})$  is 1:2. The reason for this drastic discrepancy lies in the considerable difference of the temperature behavior of the two Debye-Waller factors,  $f(\text{cation})$  and  $f(\text{anion})$ . At 4.2 K the crystallographic result for the ratio  $\text{Fe}(\text{cation}):\text{Fe}(\text{anion})$  is much better reflected by the corresponding Mössbauer absorption areas  $A_1$  and  $A_2$  (Fig. 1). Thus we conclude that the ratio of different iron sites within a compound is not reflected in a Mössbauer measurement at one single temperature only.

X-ray studies which were obtained at room temperature and at 225 K indicate peculiar structural properties of the anion (Fig. 3). Three of the four CO-groups exhibit mean-square displacements

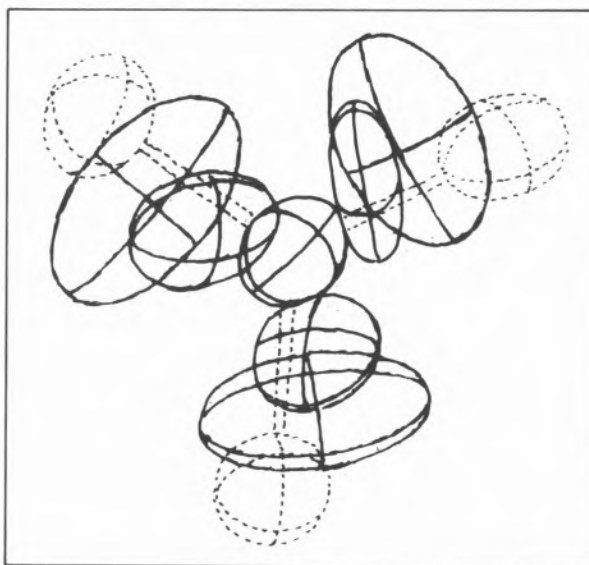


Fig. 3

ORTEP-plot of the anion projected onto the plane of the three static CO-groups. The picture indicates that the fourth CO-group is distributed equally between three equivalent positions

which may be considered as normal. The fourth CO-group, however, turns out to occupy — with equal probability — three equivalent positions,

each of them being characterized by large mean-square displacement. Similar to this the central iron undergoes relatively large displacements. The symmetry of the three equal CO-positions is such that the weighted average of the three corresponding electric field gradient tensors yields zero-quadrupole splitting. (This conclusion is also in agreement with results which we have derived from corresponding semiempirical molecular orbital calculations). From this consideration and from the temperature-dependence of our Mössbauer parameters, we conclude that the structure of the anion is, with respect to the nuclear lifetime of  $^{57}\text{mFe}$ , static with low point-symmetry below 180 K. Above 210 K one of the four CO-groups undergoes fast enough transitions between the three equivalent positions. We have analyzed this specific dynamic behavior in full detail by inspecting the temperature dependence of the Mössbauer lineshape of  $[\text{HFe}(\text{CO})_4]^-$  under relaxation conditions [3,4]. We have found that the relaxation of one of the four CO-groups among its three equivalent sites is associated with a corresponding jump behavior of Fe; however, the triangular displacement body of Fe with jump distance of about 0.30 Å is considerably smaller than that of the CO group.

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#### SPIN-CROSSOVER DYNAMICS IN MODEL-COMPOUNDS FOR HEME PROTEINS

Besides oxygenation and carboxylation of myoglobin and hemoglobin also electron transfer reactions of heme proteins are often associated with a change of the spin state of iron from high-spin to low-spin and vice versa. Investigating this transition may yield information about how the spin-crossover mechanism determines the reaction rate. Fe(II) complexes with hexadentate ligands of the type given in Fig. 1 may serve as appropriate models, because they exhibit spin-crossover beha-

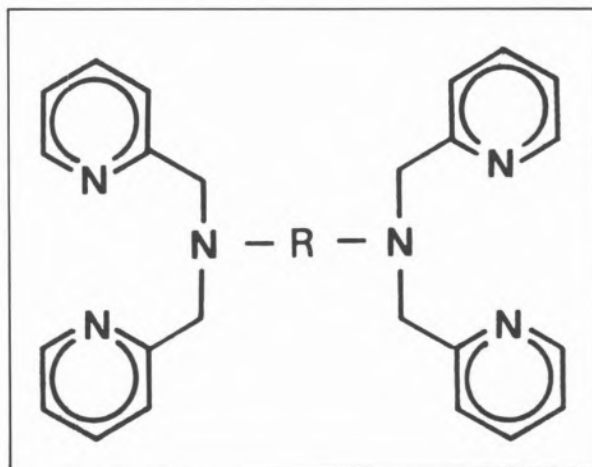


Fig. 1  
The tetrakis(2-pyridyl-methyl)-R ligand type