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 ^{57m}Fe, 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 $[HFe(CO)_4]^-$ 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.

ACKNOWLEDGEMENTS

This work was supported by Deutsche Forschungsgemeinschaft.

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PS4.12 — MO

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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-

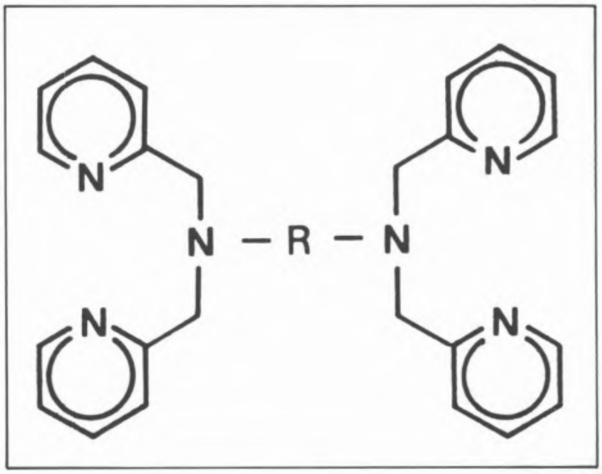

Fig. 1
The tetrakis(2-pyridyl-methyl)-R ligand type

vior in the temperature range $100\ K \leq T \leq 400\ K$ as identified by magnetic susceptibility measurements [1]. We have performed experimental Mössbauer studies on $Fe_{0.1}Zn_{0.9}$(tpchxn) $(ClO_4)_2 \cdot nH_2O$ (tpchxn = tetrakis(2-pyridyl-methyl)-trans-1,2-cyclohexadiamine), where the transition rates are expected to fall into the time window of ^{57}Fe Mössbauer spectroscopy because according to GÜTLICH [2] dilution of ferrous spin-crossover systems with Zn causes in general an enhancement.

In Fig. 2 some representative Mössbauer spectra are displayed. At 100 K clearly two doublets can be distinguished: 1) with $\Delta E_Q = 0.48\ mms^{-1}$ and $\delta^* = 0.42\ mms^{-1}$ from low-spin Fe(II); 2) with $\Delta E_Q = 3.63\ mms^{-1}$ and $\delta^* = 0.96\ mms^{-1}$ from high-spin Fe(II). At 250 K an additional line is discernible which may be attributed to a third doublet 3) with $\Delta E_Q = 1.40\ mms^{-1}$ and $\delta^* = 0.03\ mms^{-1}$. (* = rel. to α-Fe).

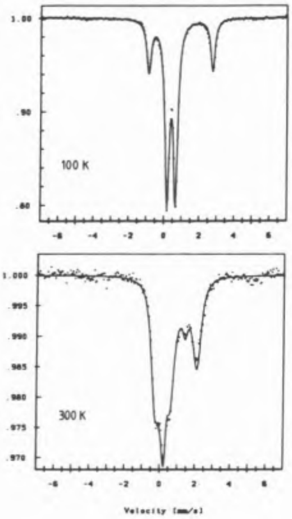
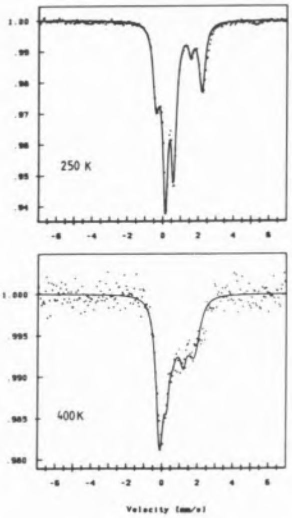

Fig. 2

Mössbauer spectra of $Fe_{0.1}Zn_{0.9}(tpchxn)(ClO_4)_2$ at four different temperatures. The solid lines are simulations with the relaxation model described in the text

The appearance of such an «intermediate site» has recently been reported by EDWARDS *et al.* [3] also for $Fe(phen)_2(NCBH_3)_2$. The Mössbauer resonances exhibit indeed line broadenings and shifts which are characteristic for relaxation processes. Therefore the attempt has been made to simulate the spectra with the random-frequency-modulation model of WICKMAN [4] which has been applied successfully by DZIOBKOWSKY *et al.* [5], *e.g.*, also to describe effects of electron hopping in the mixed-valence complex $[Fe(II)Fe(III)_2O(CH_3COO)_6(H_2O)_3]$. Common to the present case is the gradual averaging of different quadrupole splittings when the temperature is raised. For the sake of simplicity the two relaxation processes LS ⇌ HS and LS ⇌ «i» were taken as completely separated from one another as sketched in Fig. 3. The results for the four spectra displayed in Fig. 2 are given in Table I, where A_I and A_{II} denote the relative portions of the two processes (Fig. 3), whereas w_I and w_{II} are the corresponding relaxation rates defined as sum of the forward and backward transition probabilities. The symbols p_{HS} and p_i represent the occupation probabilities of the HS- and «i»-state. The temperature dependence of ΔE_Q is shown in Fig. 4. The isomer shift of the LS-doublet is nearly constant

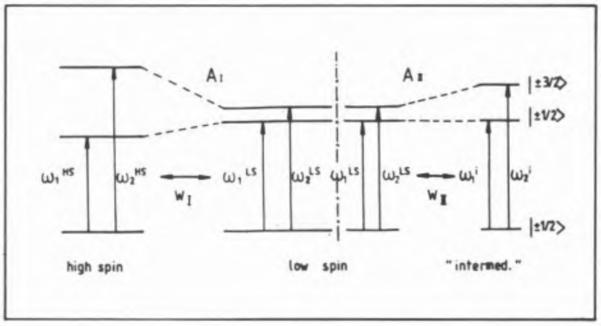

Fig. 3

Scheme of the assumed relaxation model

Table I

Relaxation parameters used for the simulations in Fig. 2 (uncertainty of about 1 in the last given digit)

T[K]	A_I	p_{HS}	w_I[MHz)	A_{II}	p_i	w_{II}[MHz]
100	1.00	0.23	0.01	0.00	—	—
250	0.86	0.41	1.1	0.14	0.41	0.06
300	0.83	0.53	3.5	0.17	0.53	0.7
400	0.75	0.58	8	0.25	0.58	0.9

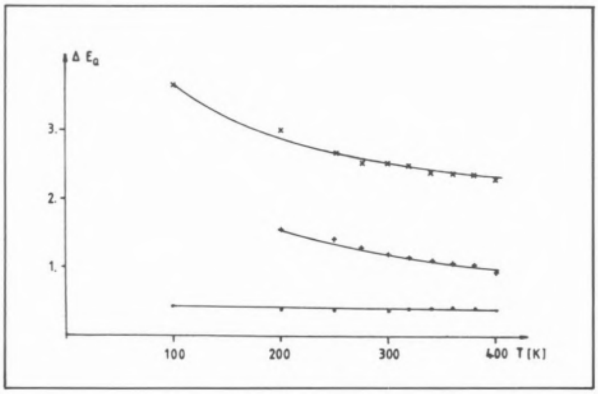

Fig. 4

Quadrupole splittings for high-spin (×) low-spin (•) and «intermediate» (+) doublet as a function of temperature

with increasing temperature while the other two doublets show a continuous decrease explainable by second order Doppler shift.

ACKNOWLEDGEMENTS

This work was supported by Deutsche Forschungsgemeinschaft.

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PS4.13 — MO

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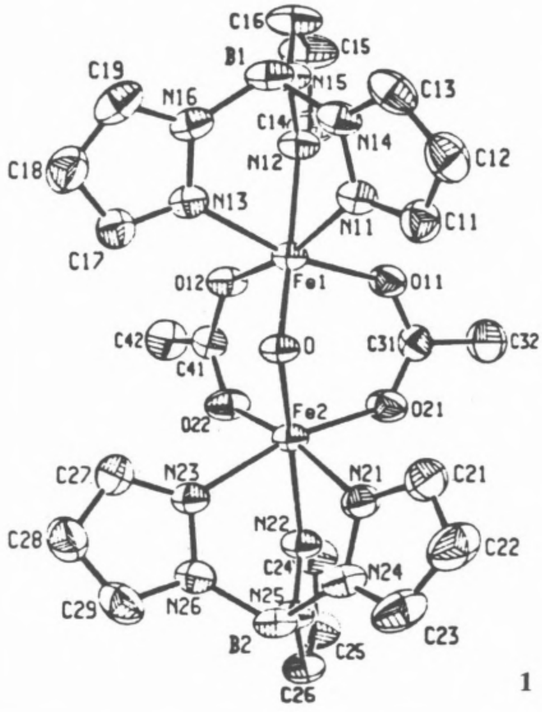
NEW CHEMISTRY OF BINUCLEAR IRON COMPLEXES — MODELS FOR HEMERYTHRIN AND RELATED PROTEINS

Previously we described the synthesis of $[Fe_2O(O_2CR)_2(HBpz_3)_2]_2$ complexes [R = Me, Et, Ph; $HBpz_3$ = hydrotris(1-pyrazolyl)borate], **1**, and showed that their magnetic and spectroscopic properties closely resemble those of the met forms of hemerythrin as well as ribonucleotide reductase [1]. The analogs where $HBpz_3$ is replaced



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