- Supplementary Information -

The temperature dependence of Mössbauer quadrupole splitting values: a quantum chemical analysis

Niklas von Rhein¹ and Vera Krewald¹

¹TU Darmstadt, Department of Chemistry, Quantum Chemistry, Peter-Grünberg-Straße 4, 64287 Darmstadt, Germany

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- Methods -

Method S1: Quantum chemical calculations. Quantum chemical calculations were performed with the unrestricted Kohn-Sham (UKS) formalism for density functional theory (DFT) using the ORCA 5.0 program suite.^{1–3} Tight convergence criteria for the energies, the integration grid "Defgrid2" in ORCA nomenclature, the Split-RI-J/RICOSX approximation⁴ with the def2/J auxiliary basis set⁵ for (meta)-GGA/hybrid functionals and the SMD model⁶ with water as solvent were applied for all calculations.

Geometry optimizations were performed with tight geometry convergence criteria in ORCA nomenclature, the TPSS functional,^{7,8} a D3 dispersion correction⁹ with Becke-Johnson damping,¹⁰ the def2-SVP¹¹ basis set on iron and carbon and the def2-TZVP¹¹ basis set on heteroatoms.

Energy calculations were performed with the OPBE functional,^{12,13} no dispersion correction, the CP(PPP)¹⁴ basis set on iron and the def2-TZVP basis set on heteroatoms.

Mössbauer parameter calculations were performed with the B3LYP hybrid functional,^{15,16} again the D3 dispersion correction with Becke-Johnson damping and the same basis sets as energy calculations. Conversion of the s-electron density $\rho(0)$ calculated by ORCA to the isomer shift δ was performed using a linear fit with equation S1¹⁷

 $\delta = a \cdot \rho(0) - b$ S1 with $a = -0,51029 \text{ mm s}^{-1} \text{ au}^3$ and $b = 6030.42944 \text{ mm s}^{-1}$ as determined by an in-house calibration study not published yet.

This in-house calibration study was also used for determining the typical error bars of theoretically calculated Mössbauer parameters. It followed the work by Gallenkamp *et al.*¹⁸ who connected low temperature experimental Mössbauer parameters to corresponding theoretical values for 20 FeN_xA_y complexes differing in spin state, oxidation state and coordination geometry. The error bars are calculated as twice the mean absolute deviation between experiment and theory. Our in-house calibration study applied mostly identical computational parameters, but instead of ORCA 4.2.1 we used ORCA 5.0.3 and, accordingly, a different integration grid (Defgrid2 in ORCA nomenclature). Also, we investigated an additional iron(III) high spin complex, [Fe(TPP)(CI)]. The calculated error bars are 0.13 mm s⁻¹ for the isomer shift and 0.22 mm s⁻¹ for the quadrupole splitting.

Method S2: Wigner Sampling. Wigner sampling¹⁹ describes a sampling method based on the normal modes of the investigated system and the Wigner distribution function. The system is displaced along each normal mode by performing the following procedure for each of them: first, the vibrational state of the normal mode is determined based on the specified temperature, a Boltzmann distribution and a random number approach. Secondly, the displacement is determined by using the vibrational state, the Wigner distribution function and again a random number approach. The details of the approach we used can be found on the SHARC 3.0 webpage.²⁰

In our work, Wigner sampling was performed using the SHARC 3.0 code.^{20–22} 600 geometries were generated at the given temperatures. Normal modes with frequencies below 10 cm⁻¹ were excluded from the sampling, which is a default setting of SHARC 3.0. The default settings of SHARC 3.0 were used in general.

Method S3: Normal coordinate conversion. The conversion from Cartesian coordinates to normal coordinates \vec{q} is done using equation S2²³

$$q_{i} = \sum_{j=1}^{3N} C_{ij}^{T} \sqrt{M_{ij}} (r_{j} - r_{j}^{0})$$
 S2

Here, \vec{r} and $\vec{r_0}$ are the distorted and the initial configuration, both being a $3N \times 1$ vector with $\langle x_1 \rangle$

 $\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix}$. M is a diagonal matrix of the atomic masses with the shape the shape 0 0 0 m_1 0 and $\boldsymbol{\mathcal{C}}$ is the normal mode matrix obtained by the frequency 0 0 0 m_1 m_1 0 0 0 0 0 0 0 0 m_2

 $\ \ 0 \ 0 \ 0 \ 0 \ \cdot./$ calculation of the initial structure.

Method S4: Normal mode fitting. Nuclear movements correlating to the Mössbauer parameters were calculated using a multicomponent fitting approach. The fit parameters b_i for each mode *i* used in the Wigner sampling approach were calculated by solving the system of equations given in equation S3 for all structures *k* in an ensemble

$$b_0 + b_1 \cdot q_{1,k} + \dots + b_{3N-P-6} \cdot q_{3N-P-6} = M_k$$
 S3

Here, M_k is the investigated Mössbauer parameter of structure k and P represents the number of modes excluded from the Wigner sampling.

Method S5: Determining the cutoff value for different electronic states. The cutoff value between the different electronic states was chosen to be $d_{x^2-y^2}(\beta) = 32$ %. This choice was made due to a relatively low density in the distribution of $d_{x^2-y^2}(\beta)$ values around that point observed at all temperatures.

- Supplementary Figures

Supplementary Figure S1: Average development of the Mössbauer parameters. The average development of the isomer shift (left panels) and the quadrupole splitting (right panels) is shown relative to the number of structures used to calculate the average. The statistical error at a given temperature is calculated with the average and the standard deviation obtained by using 600 structures.



Supplementary Figure S2: High correlation nuclear movement of the isomer shift. The nuclear movements correlated to the isomer shift calculated by a multicomponent fit of the normal coordinates are shown at three temperatures in the upper part of the figure. In the lower part, the fit parameters are shown as bar diagrams.



Supplementary Figure S3: High correlation nuclear movement of the quadrupole splitting. The nuclear movements correlated to the quadrupole splitting calculated by a multicomponent fit of the normal coordinates are shown at three temperatures in the upper part of the figure. In the lower part, the fit parameters are shown as bar diagrams.



- Supplementary Table

Supplementary Table S1: Single point energies of [Fe(TPP)(2-MeHIm)] with different multiplicities. For all total multiplicities 2S+1, the final single point energies (FSPE) and the Mulliken spin population (Mull) on the iron atom are given for geometry optimization and single point calculation. For the single point calculation, the relative spin state energies E_{Rel} are also given relative to the high spin ground state.

	Geometry optimization		Sing	le point calculat	ion
2S+1	FSPE / Ha	Mull (Fe)	FSPE / Ha	E _{Rel} / kcal mol ⁻¹	Mull (Fe)
1	-3441.4880	0.00	-3441.9734	7.4	0.00
3	-3441.4859	2.15	-3441.9823	1.8	2.41
5	-3441.4682	3.87	-3441.9851	0.0	4.02

- Supplementary Files -

Supplementary File "Ensemble Data.xlsx": Electronic and Mössbauer properties of all structures together with the displacements along all normal modes, correlation coefficients and fit parameters. In the tables "{Temperature}-Data", electronic and Mössbauer data are shown for all 600 structures the ensemble of the given temperature together with their averages and their standard deviations. Shown are final single point energy (FSPE) in Ha, Mulliken spin population on the iron atom (Mull (Fe)), the orbital occupations of the α - and β -d-orbitals in %, the components of the diagonalized electric field gradient V_{xx} , V_{yy} and V_{zz} in a.u.⁻³, the asymmetry factor η , the isomer shift δ in mm s⁻¹ and the quadrupole splitting ΔE_Q in mm s⁻¹. In the tables "{Temperature}-Normal_Modes", the isomer shift, the guadrupole splitting and the displacement along each normal mode are shown for all 600 structures in the ensemble at the given temperature. Furthermore, the Pearson R² of the isomer shift and the quadrupole splitting depending on the displacement along each normal mode and the fit coefficients of the multicomponent fit are shown. Also, the R² of the Mössbauer parameters to the calculated nuclear movement are shown. Note, that for the first six normal modes corresponding to translational and rotational movement, all values are chosen as 0. Furthermore, for the seventh mode not used in the linear fit because of having a frequency below 10 cm⁻¹, the fit coefficient is also chosen 0.

Supplementary Files "{Temperature}-geometries.xyz": .xyz-data for all structures of the ensemble created at the given temperature. The geometries are given in an ORCA-readable format with the number of atoms followed by a comment followed by the atom coordinates. The structures are not separated by empty lines.

Supplementary File "FeTPP2MeHIm_c0m5.xyz": Optimized geometry of [Fe(TPP)(2-MeHIm)]. The optimized geometry of the [Fe(TPP)(2-MeHIm)] complex is given in an ORCA-readable format.

Supplementary File "FeTPP2MeHIm_c0m5.molden": Vibrational mode data of [Fe(TPP)(2-MeHIm)]. The vibrational data is given in the .molden format.

Supplementary File "FeTPP2MeHIm_c0m5-{Mössbauer parameter}.molden": Nuclear movement correlating to the given Mössbauer parameter. The vibrational movements for the given Mössbauer parameters are given for each temperature in the .molden format. Note that the entry "Frequency" in the .molden format corresponds to the temperature of the nuclear movement.

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