

SUPPORTING INFORMATION

Title: A Ferromagnetically Coupled Diiron(III) Complex with a *m*-Phenylenediamine-Based Ligand

Author(s): Biplab Biswas, Sunita Salunke-Gawali, Thomas Weyhermüller, Vinzenz Bachler, Eckhard Bill, Phalguni Chaudhuri*

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$$\hat{H}_Q = eQV_{zz}/4I(2I-1)\left[3\hat{I}_z^2 - I^2 + \eta(\hat{I}_x^2 - \hat{I}_y^2)\right]$$

Equation S3

where Q is the quadrupole moment and V_{zz} and η are the main component and the asymmetry parameter of the electric field gradient tensor. In zero-field condition the quadrupole splitting is given by

$$\Delta E_Q = eQV_{zz}/2\sqrt{1+\eta^2/3}$$

Equation S4

Experimental Section

Spectroscopic techniques: Magnetic susceptibility data were measured from powder samples of solid material in the temperature range 2 - 300 K at a field of 1.0 T by using a SQUID susceptometer (MPMS-7, Quantum Design). Multiple-field variable-temperature magnetization measurements were done at 1, 4, and 7 T also in the range 2 - 300K with the magnetization equidistantly sampled on a 1/T temperature scale. The experimental data were corrected for underlying diamagnetism by use of tabulated Pascal's constants. The susceptibility and magnetization data were simulated with our own package julX for exchange coupled systems written by E.B. The simulations are based on the usual spin-Hamilton operator for di-nuclear ferric complexes with spin $S_1 = S_2 = 5/2$:

$$\begin{aligned} \hat{H} = & -2J[\hat{S}_1 \cdot \hat{S}_2] + g\beta(\hat{S}_1 + \hat{S}_2) \cdot \vec{B} \\ & + \sum_{i=1,2} D_{Fe} [\hat{S}_{i,z}^2 - 1/3 S(S+1)] + E/D_{Fe} (\hat{S}_{i,x}^2 - \hat{S}_{i,y}^2) \end{aligned}$$

Equation S1

where g_{Fe} is the average electronic g value of the ferric ions, and D_{Fe} and E/D_{Fe} are the axial zero-field splitting and rhombicity parameters. The magnetic moments were obtained from the first order derivative of the eigenvalues of eq. 1. Intermolecular interactions could be considered by using a Weiss temperature, Θ_w , as perturbation of the temperature scale, $kT' = k(T - \Theta_w)$ for the calculation. Powder summations were done by using a 16-point Lebedev grid.

Mössbauer data were recorded on a spectrometer with alternating constant acceleration. The minimum experimental line width was 0.24 mms^{-1} (full width at half-height). The sample temperature was maintained constant either in an Oxford Instruments Variox or an Oxford Instruments Mössbauer-Spectromag cryostat. The latter is a split-pair super-conducting magnet system for applied fields up to 8T where the temperature of the sample can be varied in the range 1.5 K to 250K. The field at the sample is perpendicular to the γ -beam. The $^{57}\text{Co/Rh}$ source (1.8 GBq) was positioned at room temperature inside the gap of the magnet system at a zero-field position. Isomer shifts are quoted relative to iron metal at 300K.

Magnetic Mössbauer spectra were simulated by using the electronic spin-Hamiltonian of eq. 1, together with the usual nuclear Hamiltonian for the hyperfine interactions of the ^{57}Fe nuclei:

$$\hat{H}_{nuc} = \hat{I} \cdot \vec{A} \cdot \hat{S} - g_N \beta_N \hat{I} \cdot \vec{B} + \hat{H}_Q$$

Equation S2

where $\hat{I} \cdot \vec{A} \cdot \hat{S}$ is the magnetic hyperfine coupling which connects S and the nuclear spin I, and \vec{A} is the hyperfine coupling tensor. The nuclear quadrupole interaction is given by

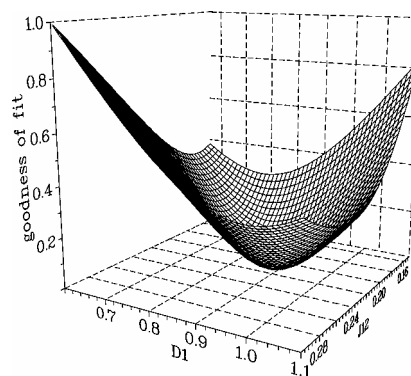


Figure S1. Error Surface for J and D_{Fe} from spin Hamiltonian simulation for the VTVH measurement of solid **1**. The goodness-of-fit is given in arbitrary units.

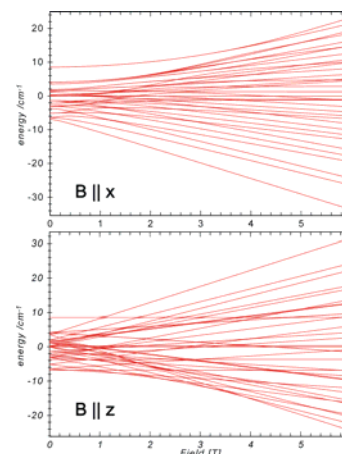


Figure S2. Energy level plots for compound **1**, as calculated with the spin Hamiltonian for a symmetric dimer (eq. 1) with $J = +0.195 \text{ cm}^{-1}$, $D_{Fe} = 0.9 \text{ cm}^{-1}$, $g_{Fe} = 2$, and for applied fields parallel to the x-axis (top) and the y-axis (bottom) of the zero-field interaction.