Supporting information for

Mössbauer and computational investigation of a functional [NiFe] hydrogenase model complex.

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Materials and Methods:

Literature methods were followed to prepare **1** and **2**.[1]

1. Mössbauer:

Mössbauer spectra were recorded on a conventional spectrometer with alternating constant acceleration of the γ-source. The minimum experimental line width was 0.24 mm/s (full width at half-height). The sample temperature was maintained constant in an Oxford Instruments Variox or in an Oxford Instruments Mössbauer-Spectromag cryostat with split-pair magnet system; the latter was used for measurements with applied field with the field at the sample being oriented perpendicular to the γ-beam. The γ-source (^{57}Co/Rh, 1.8 GBq) was kept at room temperature. By using a re-entrant bore tube the γ-source could be positioned inside the gap of the magnet coils at a position with zero field. Isomer shifts are quoted relative to iron metal at 300 K. Mössbauer spectra at zero field were collected for powder samples (ca. 50 mg) at 80 K. The Mössbauer spectra recorded at zero field were fitted using the program MFIT with Lorentzian doublets. Magnetic Mössbauer spectra were simulated with the program MX.

2. Computational details:

2.1. Geometry Optimization

Geometry optimizations were carried out using DFT with the BP86 functional[2] in combination with the resolution of identity (RI) approximation.[3] The geometry optimizations used to determine the geometric parameters were carried out using the def2-TZVP[4,5] basis set for all the atoms while the geometry optimizations used to calculate the mechanism were carried out using the def2-TZVP(-f)[6] for the metals and all the coordinating atoms and the def2-SVP[4] for the other atoms. Solvation effects were accounted for using the Conductor-like Screening Model (COSMO);[7,8] the solvent is treated as a continuum with a permittivity corresponding to that of acetonitrile (ε = 36.6). The ZORA approximation has been applied to account for scalar relativity. The nature of all stationary structures was characterized by frequency calculations (two-sided numerical differentiation).

2.2 Single Point Energy Calculations.

Final electronic energies were obtained by means of single point calculations (SP) using DFT, employing the B3LYP functional.[9,10,11,12,13] The def2-TZVP(-f)[6] at the metals and all the coordinating atoms and the def2-SVP[4] for the other atoms and the RIJCOSX approximation[14,15] were used in all single point calculations. All calculations were performed using the ORCA program package (versions 2.9 and 3.0).[16]

2.3 Gibbs Free Energy in Solution.

Energies discussed in the following sections are all Gibbs free energies at 298.15 K. These were calculated by combining the electronic energy computed by means of SP energy calculations (e.g., $Ee_{l/solv}{}^{B3LYP}$) with the thermochemical corrections evaluated at the geometry optimization level of theory ($(G - E_{el})^{BP86/opt}$). Solvation effects were accounted for using COSMO (ε = 36.6) in the SP calculations. Specifically, the Gibbs free energy is computed as $G = E_{el/solv}{}^{DFT/SP} + (G - E_{el})^{BP86/opt}$.

2.4 Calculation of the Mössbauer-parameters:

For computation of the Mössbauer parameters nonrelativistic single point calculations were carried out employing the B3LYP functional in combination with the CP(PPP) basis set for the iron and the def2-TZVP[4,5] basis set for all the other atoms. The geometry used for these calculations was taken from the atomic coordinates gained from the optimized geometry with BP86 and the def2-TZVP basis set. The crystal environment was coarsely approximated by use of the COSMO model[7,8] with acetonitrile (ε = 36.6) as the solvent. The Mössbauer isomer shifts referenced to α-iron at room temperature were

calculated from the computed electron densities at the iron center using the expression $\delta[mm/s] = \alpha(\rho - C) + \beta$ with $\alpha = -0.369$ (mm/s)/a_0^3, $\beta = 2.863$ mm/s and $C = 11810$ electrons/a_0^3 (where a_0 is the Bohr radius), proposed by Römelt et al.[17]

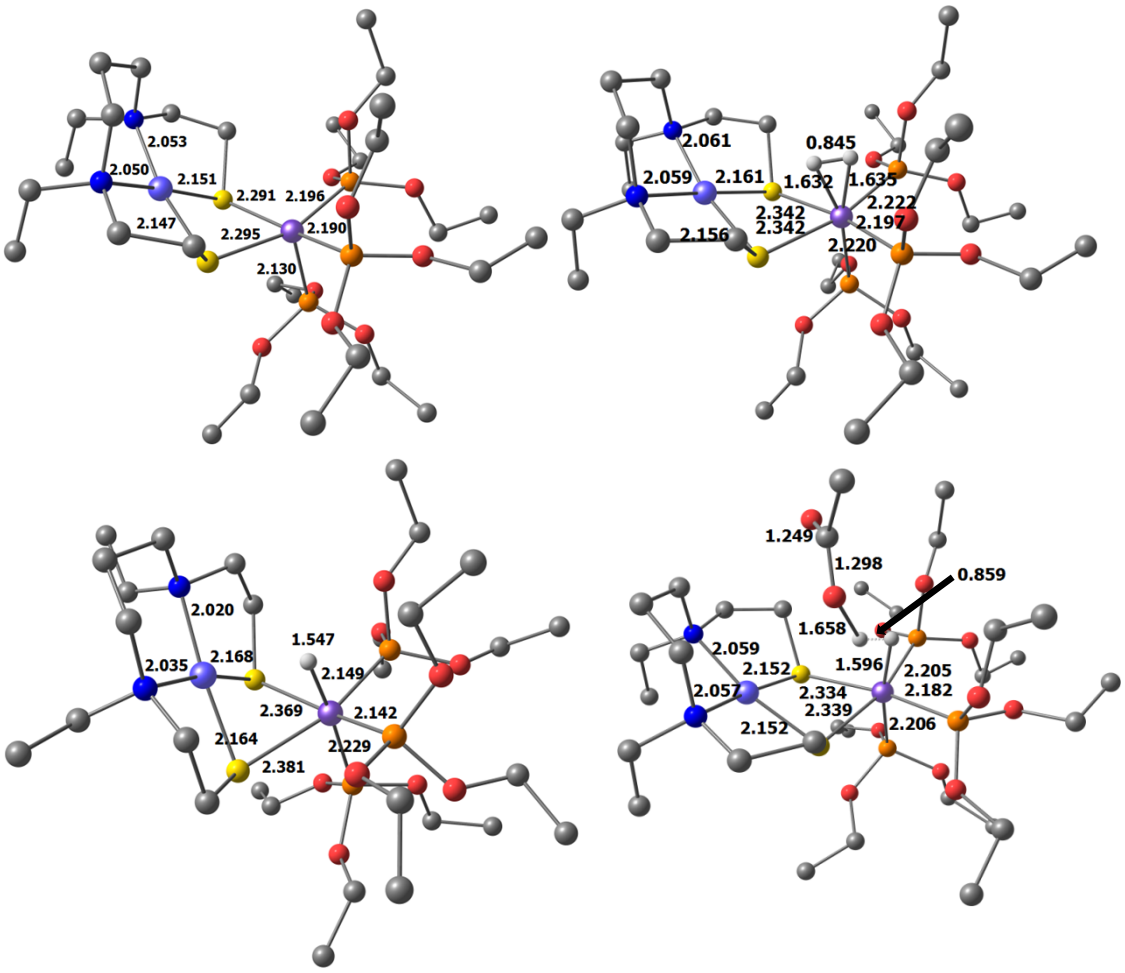


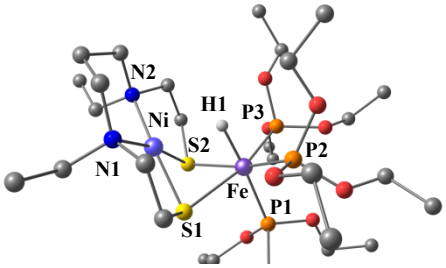
Figure S1. Geometry optimized structure of **1(-CH_3CN)**, **1-H_2**, **D-labeled-2** and of the transition state **1-H_2-CH_3COO^-** and selected bond distances. H atoms are omitted except those of the hydride or H_2 for clarity.

Table S1. Comparison of experimental and calculated first coordination sphere bond lengths and angles (Å and º) for **1** and **2**.[a]

Bond angle	**1** (exp)	**1** (calc)	**2** (exp)	**2** (calc)
Fe-P1	2.1812(9)	2.227	2.194(1)	2.229
Fe-P2	2.182(1)	2.202	2.116(1)	2.142
Fe-P3	2.195(1)	2.227	2.141(1)	2.149
Fe-S1	2.341(1)	2.348	2.366(1)	2.381
Fe-S2	2.340(1)	2.373	2.3560(9)	2.369
Ni-S1	2.1599(9)	2.150	2.1763(9)	2.164
Ni-S2	2.167(1)	2.158	2.1848(9)	2.168
Ni-N1	2.046(3)	2.067	2.007(3)	2.035
Ni-S2	2.015(3)	2.056	1.995(3)	2.020
Fe-H1	-	-	1.57(5)	1.547
Ni-H1	-	-	2.16(4)	2.301
Ni-Fe	3.3189(6)	3.395	2.7930(6)	2.883
Ni-S1-Fe	94.93(4)	97.95	75.76(3)	78.61
Ni-S2-Fe	94.79(4)	96.98	75.82(3)	78.79

[a] DFT: RI-BP86/def2-TZVP

Atom numbering used:



We note that the calculated Ni-H distance for **2** is larger than the Ni-H distance from the X-ray experiment. We imagine, however, that the electron density map from X-ray crystallography with Ni(II) (26 electrons) and Fe(II) (24 electrons) can provide only an approximate position of the hydride (2 electrons) and therefore feel that the position of the hydride from the DFT calculation of **2**, as additionally experimentally verified by the Mössbauer parameters, provides a better determination of the location of the hydride.

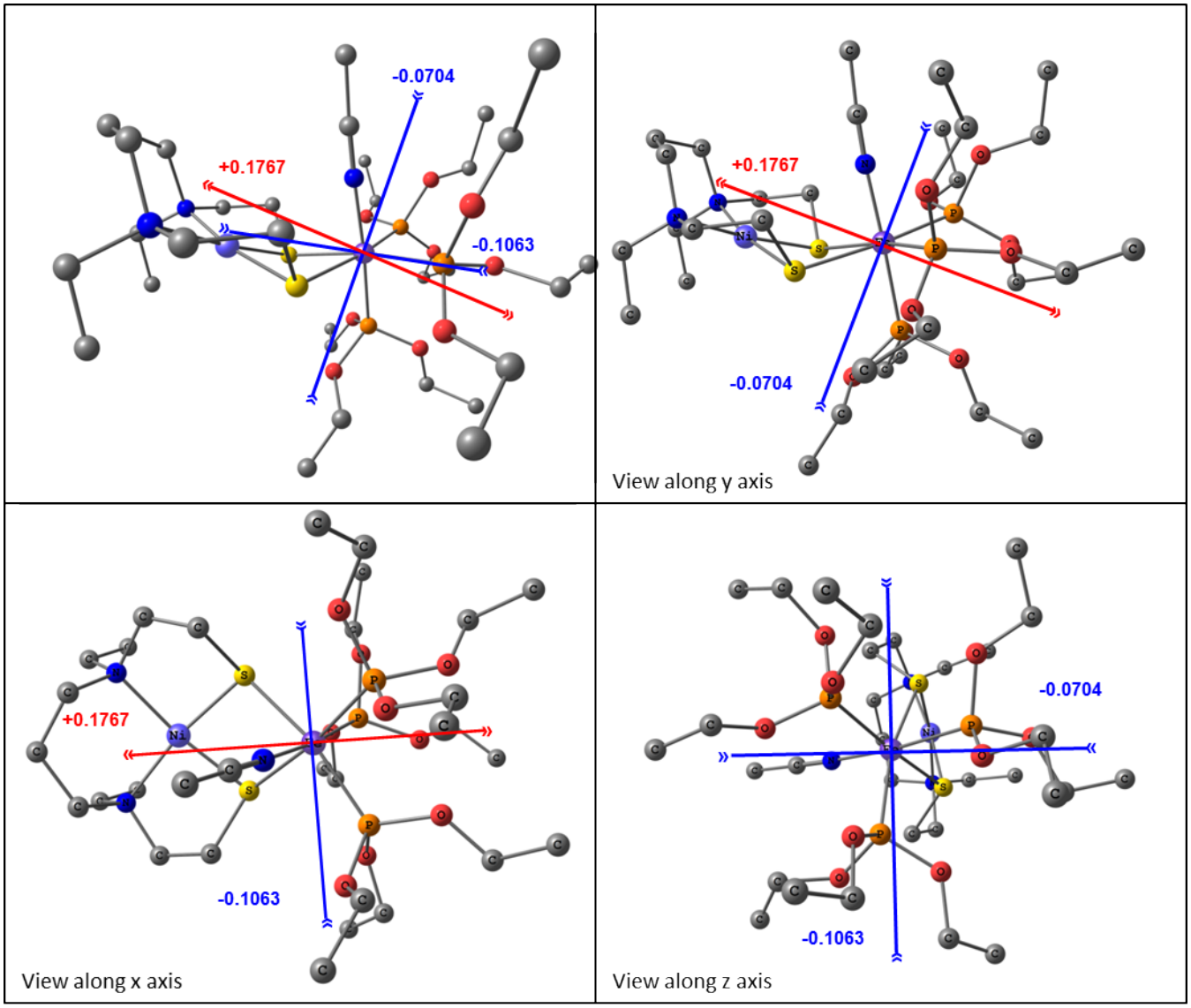


Figure S2. Orientations of the electric field gradient tensors in the molecular structure in **1** calculated using B3LYP-DFT.

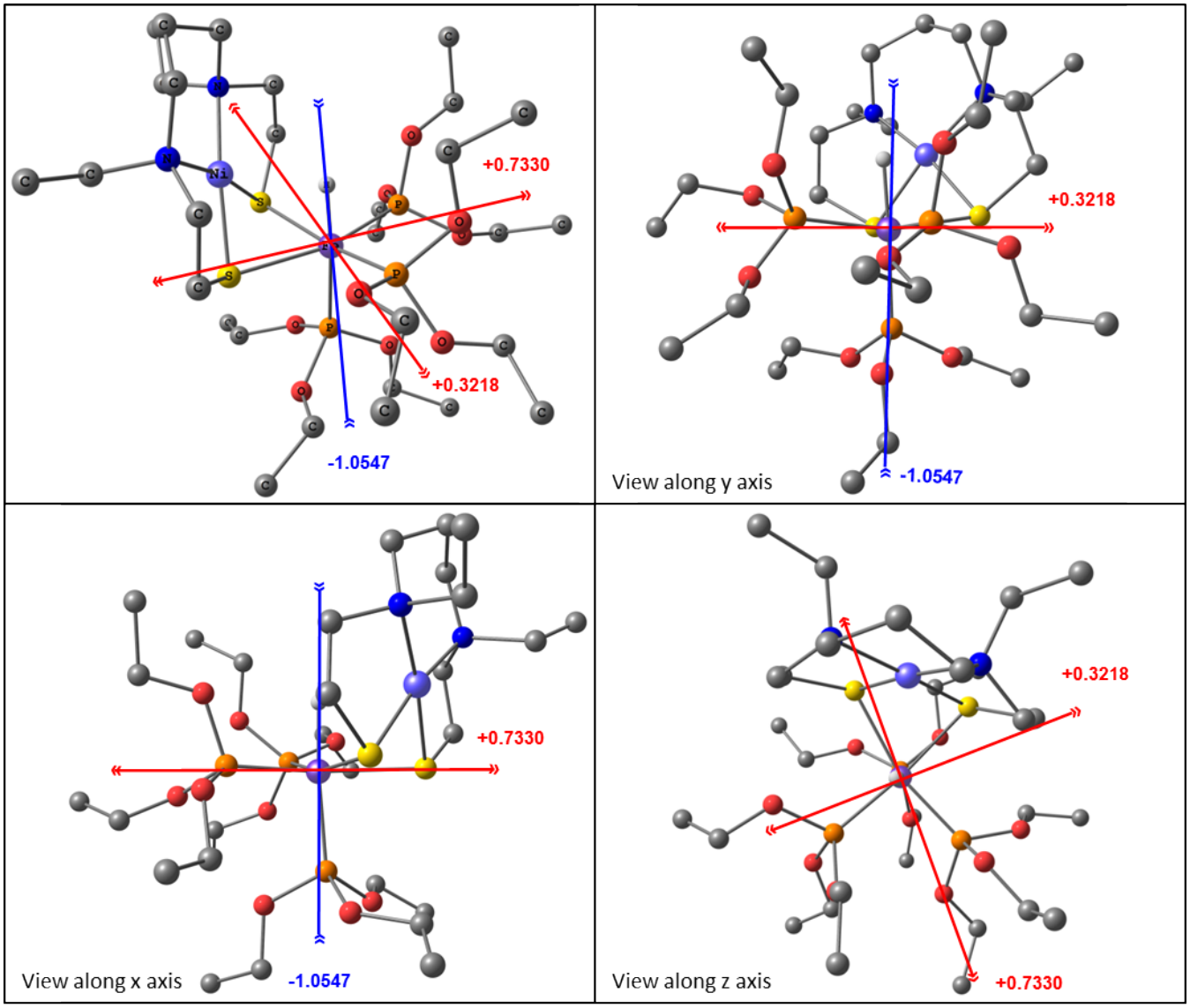


Figure S3. Orientations of the electric field gradient tensors in the molecular structure in **2** calculated using B3LYP-DFT. Note that the principal axis with the largest absolute principle value (in blue) is oriented along the Fe-H direction.

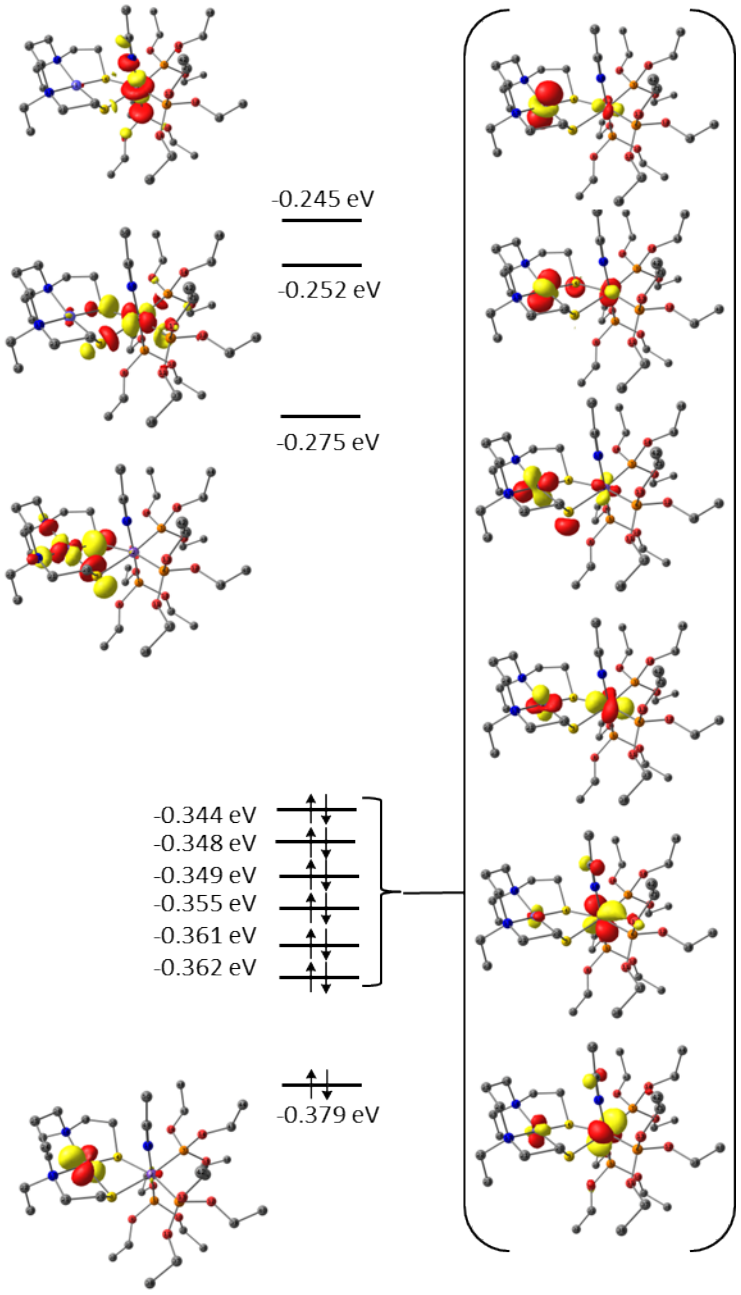


Figure S4. Calculated frontier orbital diagram for **1** with pictorial representations included (BP86/def2-TZVP/def2-TZVP/ZORA). While the complex has the symmetry to form the σ metal-metal bonds, **1** adopts a $(Fe_{nb})^6(Ni_{nb})^8$ configuration without overlap between the orbital of the two metal, in agreement with the calculated Mayer bond order which is below 0.1.

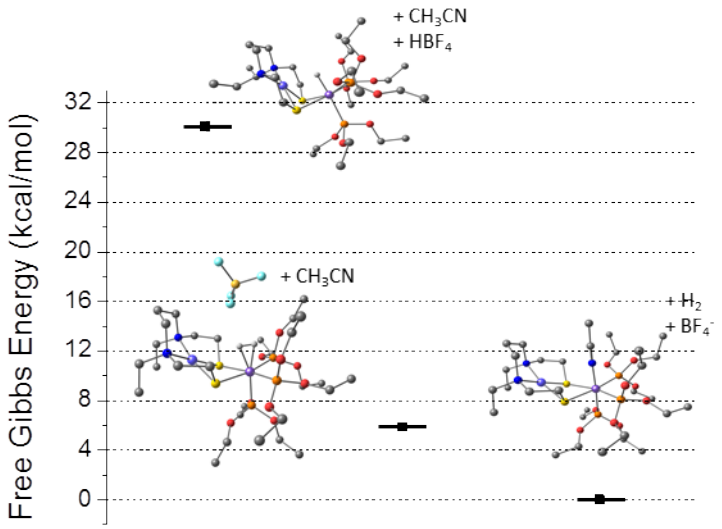


Figure S5. Free Gibbs energy H_2 production pathway calculated for **2**.

The Mössbauer spectra of **1** and **2** recorded with an applied field of 4.0 T at 4.2 K are shown in Figure S6-a and Figure S6-b respectively. Simulation of the spectrum of **1** and **2** yield a positive and a negative sign respectively for the main component V_{zz} of the electric field gradient. Under this conditions, the Mössbauer parameters are δ = 0.25 mm/s, ΔE_Q = 0.24 mm/s, η = 0.3 ± 0.3 for **1** and δ = 0.18 mm/s, ΔE_Q = -1.52 mm/s, η = 0.4 ± 0.1for **2**. In both cases, the asymmetry parameter is relatively small and the sign of ΔE_Q is significant.

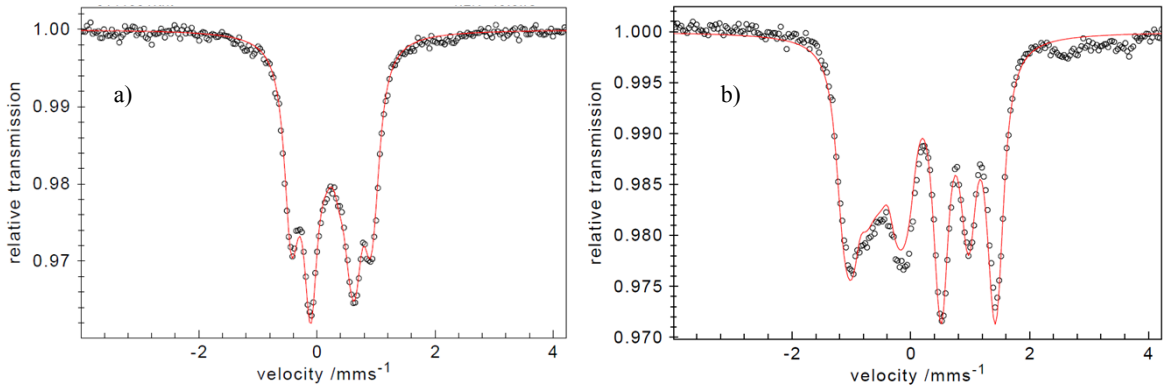


Figure S6. Mössbauer spectrum of **1** and **2** recorded with an applied field of 4.0 T at 4.2 K. The red line is the simulation for S = 0 with the parameters given in Table 1.

Coordinates of optimized structures:

1:

28	-0.025317000	-0.022194000	-0.069155000
26	3.369779000	0.029550000	-0.012680000
16	1.518639000	1.473645000	-0.031927000
16	1.531187000	-1.172659000	0.884874000
15	3.772896000	0.578394000	2.107841000
15	4.695416000	1.612241000	-0.779921000
15	4.919792000	-1.569927000	0.005653000
8	2.705221000	1.514974000	2.898828000
8	3.721733000	-0.723341000	3.062813000
8	5.212791000	1.271699000	2.366305000
8	4.310464000	3.046959000	-0.136044000
8	6.271550000	1.331850000	-0.574179000

8	4.555580000	2.021864000	-2.361117000
8	5.540109000	-1.743235000	-1.487897000
8	6.309389000	-1.547655000	0.832684000
8	4.217543000	-2.983769000	0.391758000
7	-1.194292000	1.241519000	-1.212483000
7	-1.208792000	-1.701279000	-0.147002000
7	2.932434000	-0.585786000	-1.751671000
6	1.099093000	2.155291000	-1.681297000
6	-0.382729000	2.457006000	-1.601302000
6	-2.474539000	1.746681000	-0.594199000
6	-2.318011000	2.335083000	0.800829000
6	-1.505303000	0.497691000	-2.478592000
6	-2.262339000	-0.816887000	-2.318786000
6	-1.527538000	-1.938874000	-1.593990000
6	-2.488110000	-1.653654000	0.649785000
6	-2.309455000	-1.318948000	2.125003000
6	-0.415400000	-2.897943000	0.327550000
6	1.067944000	-2.745167000	0.062475000
6	2.664875000	2.975851000	2.845049000
6	1.895692000	3.470374000	4.052147000
6	3.161236000	-0.786078000	4.418417000
6	3.397804000	-2.179091000	4.959989000
6	5.721296000	1.551234000	3.713725000
6	6.903431000	2.489411000	3.602929000
6	4.739093000	4.364143000	-0.626441000
6	3.661366000	5.382018000	-0.319965000
6	7.334406000	2.329487000	-0.711411000
6	8.656779000	1.612796000	-0.879815000
6	5.280394000	1.344137000	-3.425594000
6	4.825392000	1.919833000	-4.751747000
6	6.892327000	-2.217208000	-1.794841000
6	6.993714000	-2.441463000	-3.288633000
6	6.528578000	-1.974200000	2.209663000
6	7.902938000	-2.605289000	2.309935000
6	4.891354000	-4.286966000	0.373627000
6	4.426093000	-5.128057000	-0.799039000
6	2.717893000	-1.018577000	-2.811347000
6	2.530244000	-1.577268000	-4.138352000
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1	1.681000000	3.072080000	-1.849943000
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1	-0.772358000	2.854698000	-2.554574000
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1	-2.908364000	2.491912000	-1.285578000
1	-1.837617000	1.620485000	1.482090000
1	-1.732892000	3.263105000	0.815896000
1	-3.313138000	2.574859000	1.199006000
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1	-2.087854000	1.166520000	-3.137599000
1	-2.463102000	-1.184311000	-3.337585000
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1	1.321176000	-2.714773000	-1.004626000
1	1.638360000	-3.558536000	0.528276000
1	2.178150000	3.264403000	1.903878000
1	3.694434000	3.361305000	2.827945000
1	0.874351000	3.068800000	4.060535000
1	2.389283000	3.185087000	4.991182000
1	1.832374000	4.567485000	4.021852000

1	2.091312000	-0.551515000	4.351492000
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1	4.469399000	-2.405830000	5.038245000
1	2.962625000	-2.255694000	5.966317000
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1	6.013741000	0.594036000	4.170848000
1	6.610644000	3.446897000	3.152160000
1	7.707140000	2.043954000	3.002047000
1	7.301992000	2.695387000	4.606057000
1	5.676243000	4.617147000	-0.112055000
1	4.929415000	4.297130000	-1.705330000
1	3.993377000	6.373726000	-0.659254000
1	2.724108000	5.145041000	-0.841525000
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1	7.119802000	2.980354000	-1.572875000
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1	5.036290000	2.995859000	-4.810869000
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1	3.746672000	1.773282000	-4.902805000
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1	8.007280000	-2.787232000	-3.537165000
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1	5.731914000	-2.668946000	2.507661000
1	6.454607000	-1.082433000	2.843121000
1	8.100027000	-2.888660000	3.353829000
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1	3.339449000	-5.283408000	-0.768505000
1	1.778678000	-2.379623000	-4.125248000
1	2.204510000	-0.803607000	-4.847793000
1	3.478076000	-2.002199000	-4.499270000

2:

28	-0.077445000	-0.006389000	0.004286000
26	2.806178000	-0.041728000	0.004633000
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16	1.200208000	-0.466209000	1.694245000
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6	-2.184312000	1.673688000	-0.944198000
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6	4.459014000	-1.906763000	3.076397000
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1	-2.268528000	-3.209700000	-0.680239000
1	-2.792654000	-0.649887000	0.958057000
1	-1.613710000	-1.010030000	2.199508000
1	-3.635057000	-3.039989000	1.007818000
1	-2.407279000	-3.447528000	2.232056000
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1	0.619823000	-2.877268000	-0.051743000
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1	4.262084000	5.513350000	-1.006000000
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1	6.363925000	1.146572000	3.340238000
1	6.324936000	2.587187000	2.297269000
1	8.192944000	0.157773000	1.891811000
1	8.671563000	1.730750000	2.567653000
1	8.161074000	1.617452000	0.868233000
1	6.500662000	-0.700263000	-2.452480000
1	6.779537000	0.046433000	-0.855825000

1	7.669185000	2.123846000	-1.993813000
1	8.605150000	0.685238000	-2.463155000
1	7.402795000	1.365315000	-3.584172000
1	2.717475000	1.280459000	-4.922147000
1	4.387796000	0.903088000	-4.431850000
1	3.026875000	3.663143000	-4.131119000
1	4.220890000	3.229650000	-5.371638000
1	4.703811000	3.272207000	-3.656866000
1	2.352464000	-1.196894000	-3.943436000
1	2.487251000	-2.330556000	-2.565659000
1	2.870460000	-3.512382000	-4.753401000
1	4.213201000	-2.407445000	-5.131717000
1	4.352435000	-3.539111000	-3.764002000
1	3.850959000	-1.029414000	3.339216000
1	5.468265000	-1.550232000	2.824186000
1	3.487264000	-3.265861000	4.459061000
1	5.115143000	-3.786528000	3.951500000
1	4.925757000	-2.445740000	5.105386000
1	5.976308000	-3.592700000	1.140926000
1	7.048584000	-2.174312000	1.138208000
1	6.662457000	-4.082694000	-1.258286000
1	8.062495000	-4.046647000	-0.160941000
1	7.733873000	-2.661308000	-1.225239000
1	3.806003000	-4.779820000	0.832039000
1	4.540119000	-4.593598000	-0.788053000
1	2.957128000	-6.510809000	-0.782242000
1	1.634492000	-5.463143000	-0.224881000
1	2.340276000	-5.228008000	-1.848185000

1-H_2:

28	0.065902000	-0.008009000	-0.194833000
26	3.384792000	0.136989000	0.129076000
16	1.516999000	1.549387000	0.146535000
16	1.575239000	-1.186236000	0.806775000
15	3.784775000	0.554571000	2.271952000
15	4.697971000	1.745355000	-0.588198000
15	4.800101000	-1.571867000	0.020173000
8	2.667171000	1.383971000	3.105468000
8	3.824147000	-0.794346000	3.149109000
8	5.178942000	1.328754000	2.539597000
8	4.313179000	3.168035000	0.069219000
8	6.277983000	1.474153000	-0.421554000
8	4.520689000	2.160219000	-2.163806000
8	4.816317000	-2.036332000	-1.536764000
8	6.395788000	-1.524284000	0.269643000
8	4.285253000	-2.836947000	0.890590000
7	-1.058604000	1.304324000	-1.313859000
7	-1.006008000	-1.725157000	-0.581760000
6	1.195124000	2.403901000	-1.448404000
6	-0.304762000	2.605305000	-1.474396000
6	-2.431267000	1.639395000	-0.786228000
6	-2.458155000	2.193598000	0.633335000
6	-1.178319000	0.695546000	-2.683097000
6	-1.864807000	-0.664058000	-2.759476000
6	-1.143648000	-1.819313000	-2.074693000
6	-2.364798000	-1.841875000	0.060640000
6	-2.386935000	-1.577623000	1.559468000
6	-0.199755000	-2.924127000	-0.137068000
6	1.288981000	-2.676530000	-0.230184000
6	2.571857000	2.843786000	3.171072000
6	1.814452000	3.212031000	4.429515000
6	3.307436000	-0.957257000	4.516551000
6	3.640749000	-2.358366000	4.978800000
6	5.739953000	1.501276000	3.886553000
6	6.843464000	2.534762000	3.823219000
6	4.810449000	4.482315000	-0.368463000
6	3.812467000	5.543227000	0.042022000

6	7.342923000	2.388588000	-0.856805000
6	8.601721000	1.590658000	-1.117011000
6	4.986732000	1.314904000	-3.255742000
6	5.044908000	2.148920000	-4.519130000
6	5.643455000	-3.130748000	-2.064765000
6	5.527630000	-3.132231000	-3.573266000
6	7.044353000	-1.248135000	1.549352000
6	8.436000000	-1.844359000	1.515412000
6	5.085048000	-4.000001000	1.294136000
6	4.276170000	-5.265577000	1.097677000
1	2.630652000	-0.150745000	-1.289872000
1	3.451772000	-0.259436000	-1.455630000

Transition state: **1-H_2-CH_3COO^-**:

28	0.134793000	-0.003917000	-0.204823000
26	3.479876000	0.141574000	0.095898000
16	1.601716000	1.535849000	0.123695000
16	1.671931000	-1.200407000	0.710063000
15	3.877684000	0.515125000	2.233005000
15	4.776763000	1.753218000	-0.598954000
15	4.875872000	-1.561783000	-0.013109000
8	2.747808000	1.284009000	3.132932000
8	4.110042000	-0.768700000	3.204739000
8	5.258278000	1.315952000	2.520550000
8	4.423471000	3.177012000	0.101444000
8	6.370010000	1.479554000	-0.426858000
8	4.646252000	2.246045000	-2.151369000
8	4.893456000	-2.076524000	-1.544364000
8	6.485210000	-1.545345000	0.234444000
8	4.369644000	-2.818067000	0.901847000
7	-1.030560000	1.339226000	-1.237922000
7	-0.945626000	-1.714878000	-0.587685000
6	1.218456000	2.440992000	-1.430122000
6	-0.282002000	2.643241000	-1.376743000
6	-2.389209000	1.651310000	-0.678928000
6	-2.396685000	2.168488000	0.755683000
6	-1.166141000	0.758588000	-2.618851000
6	-1.868568000	-0.593384000	-2.707460000
6	-1.136868000	-1.773485000	-2.077158000
6	-2.271948000	-1.851191000	0.102506000
6	-2.237184000	-1.612519000	1.606283000
6	-0.113886000	-2.921141000	-0.212408000
6	1.368698000	-2.657570000	-0.362618000
6	2.585121000	2.731686000	3.130878000
6	1.274807000	3.059878000	3.815440000
6	3.077919000	-1.534521000	3.888413000
6	3.690279000	-2.166570000	5.123172000
6	5.781251000	1.487198000	3.874451000
6	6.787257000	2.619815000	3.860923000
6	4.923403000	4.480658000	-0.326919000
6	3.986153000	5.553145000	0.190338000
6	7.424496000	2.357941000	-0.921106000
6	8.651965000	1.527127000	-1.237304000
6	4.993134000	1.383220000	-3.276370000
6	5.217746000	2.260120000	-4.492031000
6	5.531592000	-3.299715000	-2.019779000
6	5.371593000	-3.356503000	-3.524427000
6	7.130249000	-1.189471000	1.487754000
6	8.527679000	-1.777140000	1.482123000
6	5.181919000	-3.952336000	1.325193000
6	4.326101000	-5.204064000	1.327468000
1	1.550022000	1.863040000	-2.300996000
1	1.742906000	3.405812000	-1.409207000
1	-0.527783000	3.259480000	-0.504086000
1	-0.652629000	3.167360000	-2.276367000
1	-2.980790000	0.733025000	-0.731274000
1	-2.876402000	2.379351000	-1.354579000

1	-1.786730000	1.528517000	1.408285000
1	-2.025482000	3.197502000	0.846233000
1	-3.428211000	2.164096000	1.134428000
1	-0.144261000	0.661590000	-3.016810000
1	-1.714123000	1.490400000	-3.241172000
1	-1.941869000	-0.826180000	-3.781794000
1	-2.912565000	-0.532940000	-2.364937000
1	-0.136150000	-1.876249000	-2.523377000
1	-1.693795000	-2.700552000	-2.308500000
1	-2.665529000	-2.860019000	-0.121867000
1	-2.963251000	-1.139440000	-0.363382000
1	-1.660297000	-2.373480000	2.146893000
1	-1.799671000	-0.633003000	1.840314000
1	-3.262689000	-1.636812000	1.999858000
1	-0.434456000	-3.773656000	-0.836464000
1	-0.339105000	-3.168036000	0.832799000
1	1.667577000	-2.455278000	-1.405564000
1	1.958850000	-3.497047000	0.029917000
1	2.602093000	3.098864000	2.095736000
1	3.437395000	3.174122000	3.670637000
1	0.430100000	2.634610000	3.257662000
1	1.254016000	2.666006000	4.840277000
1	1.145440000	4.150739000	3.864405000
1	2.704515000	-2.294475000	3.187372000
1	2.250637000	-0.861587000	4.152070000
1	4.530628000	-2.823824000	4.859892000
1	4.049816000	-1.402510000	5.825481000
1	2.931761000	-2.774588000	5.638314000
1	4.949253000	1.694975000	4.564084000
1	6.244379000	0.538606000	4.182857000
1	6.320060000	3.564340000	3.551448000
1	7.619373000	2.403250000	3.178043000
1	7.200424000	2.756436000	4.870390000
1	5.932442000	4.614361000	0.090287000
1	4.986506000	4.499957000	-1.423615000
1	4.363892000	6.542934000	-0.104863000
1	2.977305000	5.437044000	-0.227707000
1	3.917747000	5.526604000	1.285947000
1	7.066012000	2.893802000	-1.812425000
1	7.641554000	3.095922000	-0.133609000
1	8.438164000	0.785396000	-2.017883000
1	9.458984000	2.183332000	-1.594076000
1	9.011392000	0.999374000	-0.344203000
1	5.895915000	0.803412000	-3.025703000
1	4.153178000	0.691601000	-3.437826000
1	6.053354000	2.957993000	-4.341950000
1	5.452397000	1.629019000	-5.361103000
1	4.314886000	2.839484000	-4.727661000
1	6.589607000	-3.289012000	-1.718609000
1	5.030755000	-4.156825000	-1.543489000
1	4.309104000	-3.316509000	-3.799440000
1	5.800728000	-4.295364000	-3.903911000
1	5.898277000	-2.522394000	-4.007168000
1	6.539470000	-1.575217000	2.332534000
1	7.146960000	-0.093397000	1.551524000
1	9.056768000	-1.485739000	2.401802000
1	8.501958000	-2.874553000	1.436722000
1	9.106239000	-1.409053000	0.623923000
1	6.052302000	-4.061351000	0.664117000
1	5.549526000	-3.730463000	2.338786000
1	3.974449000	-5.450842000	0.316600000
1	4.915777000	-6.054508000	1.699632000
1	3.453211000	-5.082909000	1.982851000
1	2.724213000	-0.150070000	-1.643707000
1	3.549141000	-0.277077000	-1.442235000
8	1.849799000	-2.289105000	-3.481807000
8	1.962132000	-0.059598000	-3.113680000

6	1.938135000	-1.107686000	-3.878332000
6	2.034804000	-0.835120000	-5.380993000
1	1.526707000	-1.623615000	-5.948814000
1	1.630117000	0.150415000	-5.643964000
1	3.096397000	-0.847684000	-5.672814000

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