Structure, electronic configuration, and Mössbauer parameters of an antiferromagnetic Fe_2-peroxo intermediate of methane monooxygenase

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Supplementary Information

Table S1. Cartesian coordinates (Å) corresponding to *final* (89 atom) optimized structure of $MMOH_{Peroxo}$. [F] indicates the six α carbons kept frozen during optimization.

Fe1	1.41860853	0.56522498	-0.44498686	
Fe2	-1.79791700	0.48082584	1.16211671	
O1	0.20451988	1.98480082	-0.29527264	
O2	-1.01306177	1.97967508	0.29850044	
C	4.63160102	3.23216076	1.82085762	[F]
C	5.48310843	2.94791130	0.56198511	
C	4.78323632	3.32429103	-0.76971292	
C	3.76191338	2.30342235	-1.26639149	
O	3.05387219	1.71141228	-0.37388045	
O	3.64905135	2.08853486	-2.52172514	
C	3.59894985	-1.71426730	3.02119706	[F]
C	3.20484455	-0.39463040	3.73304922	
C	1.68132906	-0.17138051	3.87063042	
C	0.96470673	0.15956913	2.54893870	
O	-0.29275543	0.35630006	2.59328004	
O	1.67656919	0.19463974	1.50928163	
C	6.15471077	-1.47847203	-1.16909993	[F]
C	4.77797766	-0.80022398	-1.10977970	
C	3.66208487	-1.79795404	-1.00308189	
N	2.34062527	-1.43026147	-0.77160067	
C	3.73635467	-3.16937281	-1.06163025	
C	1.63311327	-2.54768568	-0.68021979	
N	2.43731298	-3.63382159	-0.85445847	
C	-5.46522674	3.62861683	-0.62363489	
C	-4.28368956	3.28400049	0.30633665	
C	-4.40198555	1.87242274	0.89464105	
O	-3.32885798	1.46822216	1.56602859	
O	-5.41798401	1.17576610	0.74073254	

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C	-3.26700617	-2.55423319	-3.06839838	[F]
C	-2.42895955	-1.31501904	-3.44484083	
C	-1.16254652	-1.18226294	-2.57996198	
C	-1.41524327	-0.66975129	-1.17137161	
O	-2.53748399	-0.28057944	-0.77551777	
O	-0.41466244	-0.60789721	-0.33813736	
C	-5.91158552	-2.83650995	1.17492647	[F]
C	-4.69753327	-1.90574357	0.97099092	
C	-3.64381482	-2.14724653	2.01348957	
N	-2.47271495	-1.39556155	2.15117963	
C	-3.66788076	-3.10341725	3.00151226	
C	-1.82077236	-1.88399551	3.19956333	
N	-2.50299068	-2.92545283	3.74732781	
O	1.40330109	0.94207904	-2.54866413	
C	-5.34384279	5.03011172	-1.27067350	[F]
H	-6.66881298	-2.63256549	0.41147123	
H	-5.62650467	-3.89316285	1.09822126	
H	-6.36862200	-2.66553252	2.15612812	
H	6.94689234	-0.72462310	-1.21893924	
H	6.32314318	-2.09248980	-0.27713324	
H	6.24405764	-2.11682858	-2.05595302	
H	5.19536761	2.98590347	2.72843301	
H	4.35960532	4.29380905	1.86490485	
H	3.71563993	2.63768342	1.79462970	
H	-6.19854401	5.22727028	-1.92727365	
H	-5.31290561	5.81210174	-0.50251473	
H	-4.42656514	5.10312015	-1.86672188	
H	-4.14919547	-2.63854713	-3.71222772	
H	-2.67322673	-3.47047216	-3.17697890	
H	-3.60910584	-2.47685711	-2.03194310	
H	4.68948888	-1.81697912	2.99063303	
H	3.18936815	-2.58018090	3.55746150	
H	3.21959171	-1.71622918	1.99762716	
H	-6.39609894	3.55764373	-0.05039596	
H	-5.52598020	2.86431557	-1.40693799	
H	-3.32441446	3.33714205	-0.22330537	
H	-4.22052883	3.99543249	1.14111853	
H	5.50995396	3.46150306	-1.57523657	
H	4.25049344	4.27757299	-0.63976525	
H	5.75872707	1.88681408	0.53631178	
H	6.41592457	3.52281959	0.62402381	
H	-2.12501693	-1.38440273	-4.49637375	
H	-3.03648155	-0.41162138	-3.33017056	

H	-0.65054874	-2.15012449	-2.49821629
H	-0.43203668	-0.49728136	-3.03012909
H	3.63896650	-0.38706229	4.74121146
H	3.62959498	0.45135542	3.18341997
H	1.19932384	-1.06257930	4.29722514
H	1.47306413	0.65813143	4.55792075
H	-4.26693475	-2.06747736	-0.02421384
H	-5.01941975	-0.85562877	1.00449359
H	4.62461308	-0.16295486	-1.98902564
H	4.72949107	-0.14281503	-0.23542822
H	-4.39428763	-3.85859827	3.23349907
H	-2.23094311	-3.45095337	4.56792124
H	-0.90245832	-1.48877725	3.58944504
H	0.57954266	-2.58762154	-0.47001869
H	2.14553015	-4.60247992	-0.83168175
H	4.56969669	-3.82687173	-1.22190034
H	0.75397399	1.65018599	-2.69378239
H	2.34515081	1.34923281	-2.72470218

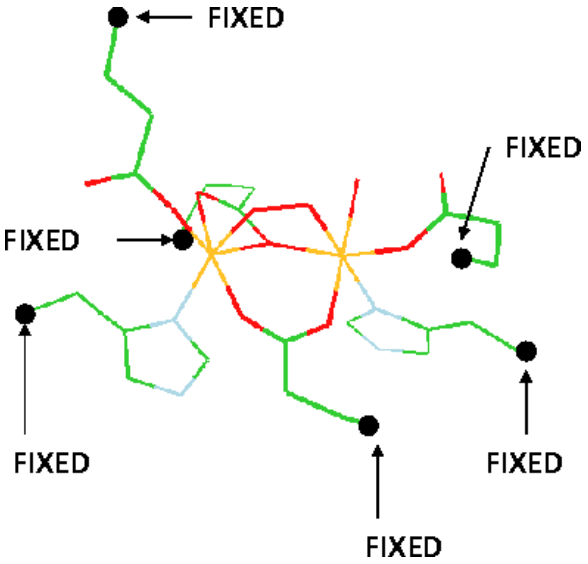

Fig. S1. Representation of skeleton of $MMOH_{peroxo}$ structure displaying the six α carbons kept frozen during optimization of *final* 89 atom model. These six carbons are labelled [F] in Table S1.

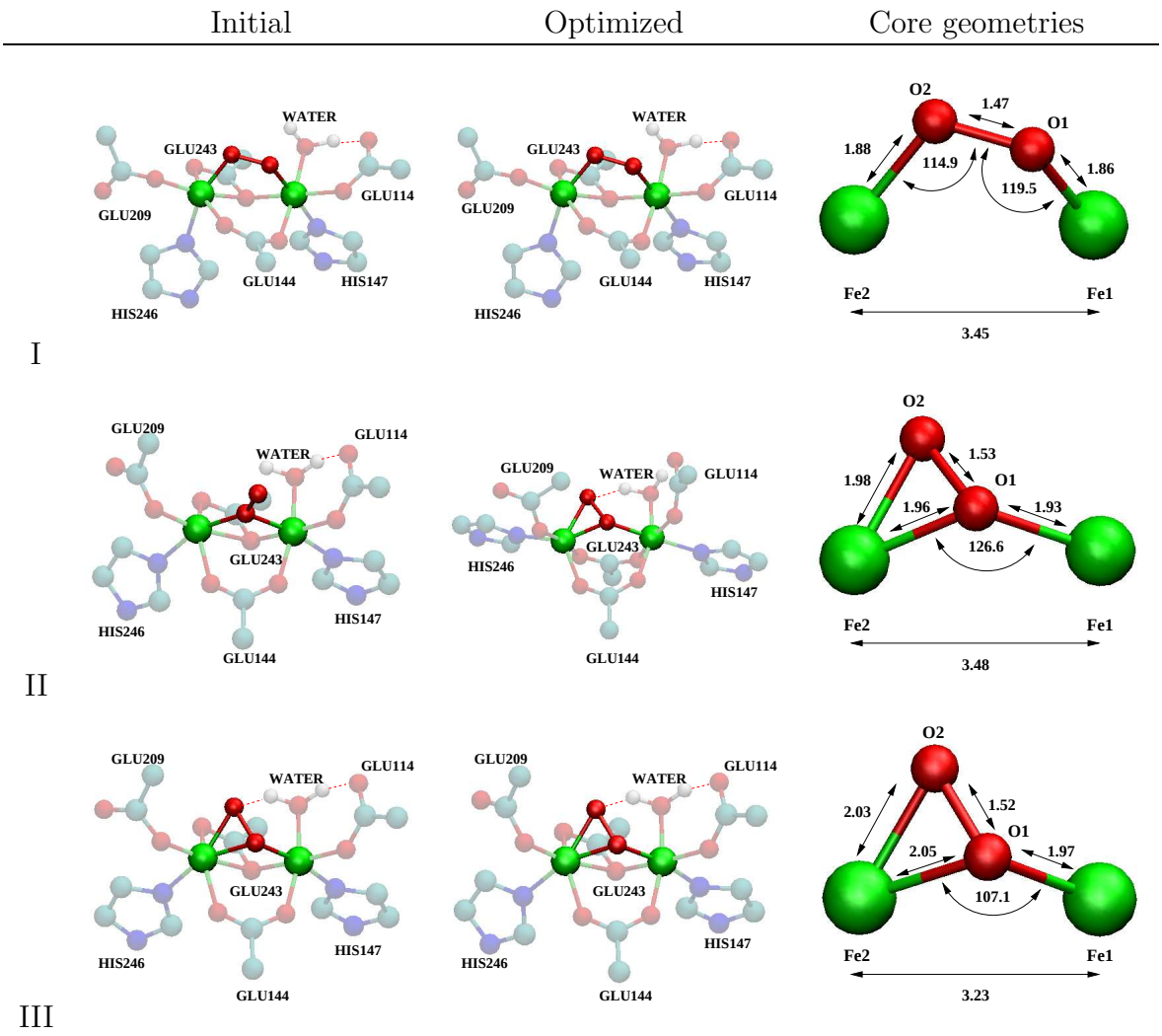

Fig. S2. Initial *feasibility* 53 atom Models I, II, and III for MMOH-O_2 used as candidate structures to test possible correlations with experimental Mössbauer parameters. All structures were optimized at the U-B3LYP level with a 6-311G* (5D, 7F) basis for iron and 3-21G* for all other atoms. The starting model for the active site was obtained from the crystallographic structure corresponding to the $MMOH_{Reduced}$ state (PDB ID: 1FYZ). The dioxygen unit was added to the model in various binding configurations as shown in the Figure.

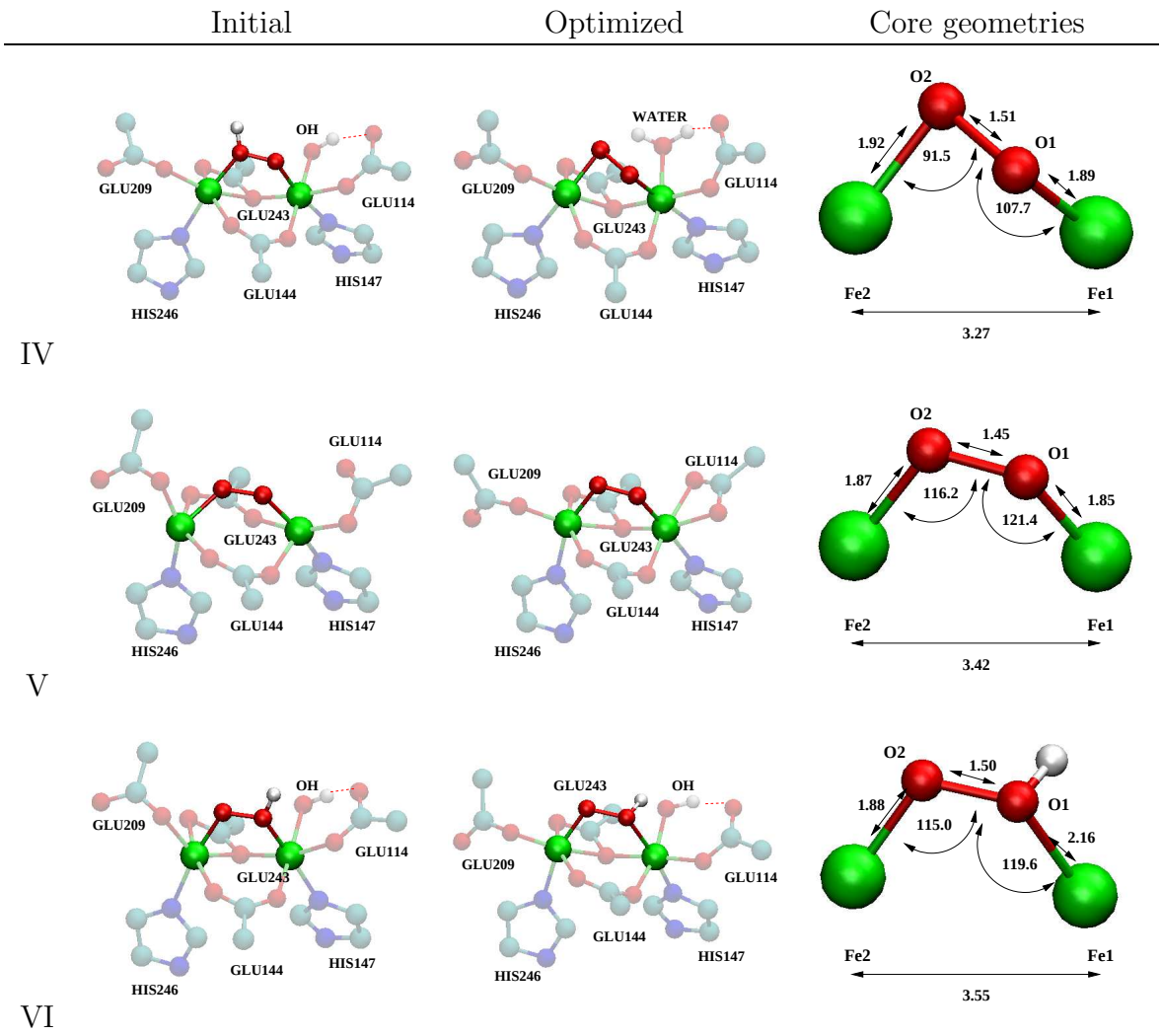

Fig. S3. Initial *feasibility* 53 atom Models IV, V, and VI for MMOH-O_2 used as candidate structures to test possible correlations with experimental Mössbauer parameters. All structures were optimized at the U-B3LYP level with a 6-311G* (5D, 7F) basis for iron and 3-21G* for all other atoms. The starting model for the active site was obtained from the crystallographic structure corresponding to the $MMOH_{Reduced}$ state (PDB ID: 1FYZ). The dioxygen unit was added to the model in various binding configurations as shown in the Figure.

Table S2. Computed isomer shifts and quadrupole splittings for initial *feasibility* 53 atom candidate structures shown in Figs. S2-S3. The geometries were optimized at the UB3LYP level with the 6-311G* (5D,7F) basis for iron and 3-21G* basis for all other atoms as described in the caption of Figs. S2-S3. After geometry optimization, an additional single point calculation at the UB3LYP level using the 6-311G* (5D. 7F) basis for all atoms was carried out to compute Mössbauer parameters.

	$\delta_{Fe}^{Computed}$ [mm/s]		$\Delta_{EQ}^{Computed}$ [mm/s]	
Structure	Fe1	Fe2	Fe1	Fe2
I	+0.57	+0.55	-1.47	-1.46
II	+0.51	+0.58	+0.60	+0.69
III	+0.50	+0.63	+0.84	+1.12
IV	+0.52	+0.57	+1.36	-1.33
V	+0.58	+0.56	-1.70	-1.56
VI	+0.50	+0.53	-1.11	-1.59

To facilitate comparison the calculated Mössbauer spectral parameters for the final 89 atom optimized structure are also shown in Table S3. These parameters have already been given in the main text Table 1.

Table S3. Computed isomer shifts and quadrupole splittings for *final* optimized 89 atom structure shown in Fig. 1 of the main text with coordinates given in Table S1. The geometry was optimized at the UB3LYP level with the 6-311G* (5D,7F) basis for the iron atoms and all atoms bound to them (see main text for further details). Other atoms used the 3-21G* basis.

	$\delta_{Fe}^{Computed}$ [mm/s]		$\Delta_{EQ}^{Computed}$ [mm/s]	
Structure	Fe1	Fe2	Fe1	Fe2
$MMOH_{Peroxo}$	+0.68	+0.66	-1.49	-1.48

Table S4. Comparison of two different methods for the computation of quadrupole splittings for *final* optimized 89 atom structure of $MMOH_{Peroxo}$ shown in Fig. 1 of the main text with coordinates given in Table S1.

Computational	$V_{zz}^{Computed}$ [a.u.][a]		$\eta^{Computed}$		Q [barn]		$\Delta_{EQ}^{Computed}$ [mm/s]	
Method	Fe1	Fe2	Fe1	Fe2	Fe1	Fe2	Fe1	Fe2
Training Set: Equation 5	1.000924	0.905132	0.533788	0.972295			-1.49	-1.48
Using Q: Equations 2 & 3	1.000924	0.905132	0.533788	0.972295	0.16	0.16	-1.69	-1.68

[a]Convertion factor of V_{zz} from a.u. to SI units: 9.717362×10^{21} V/m^2.

Table S5. For comparison, predicted electric field gradients for members of the training set making use of Eqs. 2 and 3 in the main text are presented. Experimental values for ΔE_Q given in Table 4 and Q = 0.16 barn have been used. In the absence of reliable values of η for some complexes, the values computed at the U-B3LYP/6-311G* level as reported in Table 4 have been used.

Complex	S	$V_{ZZ}^{\text{Predicted from Eqs.2–3}}$ [a.u.][a]
$CpFe(CO)_2Cl$	0	−1.111523
$Fe(CO)_3$(1,4-butadiene)	0	+0.824907
$Fe(CO)_3$(*cycle*-butadiene)	0	−0.939743
$Fe(CO)_5$	0	−1.558464
FeO_4^{2-}	1	−0

[a]Convertion factor of V_{zz} from a.u. to SI units: 9.717362×10^{21} V/m^2.