A DFT study of structure and electrochemical properties of diiron-hydrogenase models with benzenedithiolato and benzenediselenato ligands

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Supporting Information

Table S1: The first and second standard reduction potentials of the $Fe_2(bdt)(CO)_6$ complex relative to ferrocene electrode computed with different density functionals (in V). For each density functional, the redox potentials of the Fc^+/Fc couple was also evaluated at the same level of theory. Geometry optimizations and energy calculations were performed with contiuum solvation model and def2-SVP and def2-TZVPD basis sets, respectively.

SRP	TPSSh	M06	M06-L	B3LYP	PBE0	Exp.[a]
E_1^o	-1.31	-1.43	-1.30	-0.89	-1.06	-1.30
E_2^o	-1.25	-1.44	-1.23	-1.40	-1.42	-1.15

[a] ref. [1, 2]

Table S2: Relative electronic energies of optimized neutral and singly reduced $Fe_2(bdt)(CO)_6$ complexes with different multiplicity (in kJ/mol). Geometry optimizations and energy calculations were performed at TPSSh/def2-SVP+COSMO and TPSSh/def2-TZVPD+COSMO levels, respectively.

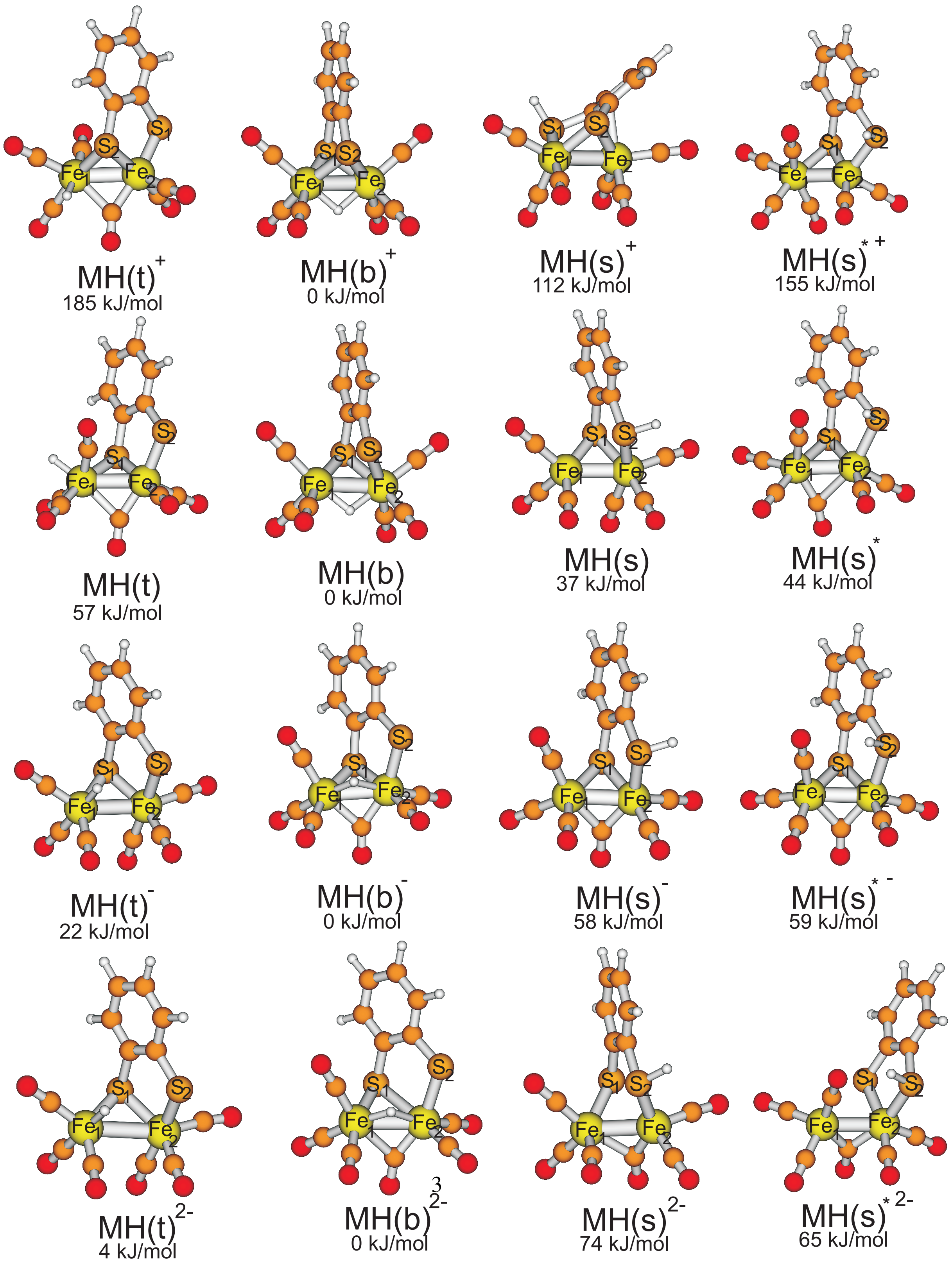
M		M^-	
Multiplicity	ΔE	Multiplicity	ΔE
1	0	2	0
3	123	4	66
5	213	6	216

References

[1] J. F. Capon, F. Gloaguen, P. Schollhammer, and J. Talarmin. Activation of Proton by the Two-Electron Reduction of a Di-Iron Organometallic Complex. *J. Electroanal. Chem.*, 595:47–52, 2006.

[2] G. A. N. Felton, A. K. Vannucci, J. Chen, L. T. Lockett, N. Okumura, B. J. Petro, U. I. Zakai, D. H. Evans, R. S. Glass, and D. L. Lichtenberger. Hydrogen Generation from Weak Acids: Electrochemical and Computational Studies of a Diiron Hydrogenase Mimic. *J. Am. Chem. Soc.*, 129:12521–12530, 2007.

Figure S1: Optimized isomers of the singly protonated complexes with the benzenedithiolato ligand and their relative free energies.



$\mathrm{MH(t)}^{+}$ 185 kJ/mol

$\mathrm{MH(b)}^{+}$ 0 kJ/mol

$\mathrm{MH(s)}^{+}$ 112 kJ/mol

$\mathrm{MH(s)}^{*\,+}$ 155 kJ/mol

MH(t) 57 kJ/mol

MH(b) 0 kJ/mol

MH(s) 37 kJ/mol

$\mathrm{MH(s)}^{*}$ 44 kJ/mol

$\mathrm{MH(t)}^{-}$ 22 kJ/mol

$\mathrm{MH(b)}^{-}$ 0 kJ/mol

$\mathrm{MH(s)}^{-}$ 58 kJ/mol

$\mathrm{MH(s)}^{*\,-}$ 59 kJ/mol

$\mathrm{MH(t)}^{2-}$ 4 kJ/mol

$\mathrm{MH(b)}^{2-}$ 0 kJ/mol

$\mathrm{MH(s)}^{2-}$ 74 kJ/mol

$\mathrm{MH(s)}^{*\,2-}$ 65 kJ/mol

Figure S2: Optimized isomers of the doubly protonated complexes with the benzenedithiolato ligand and their relative free energies.

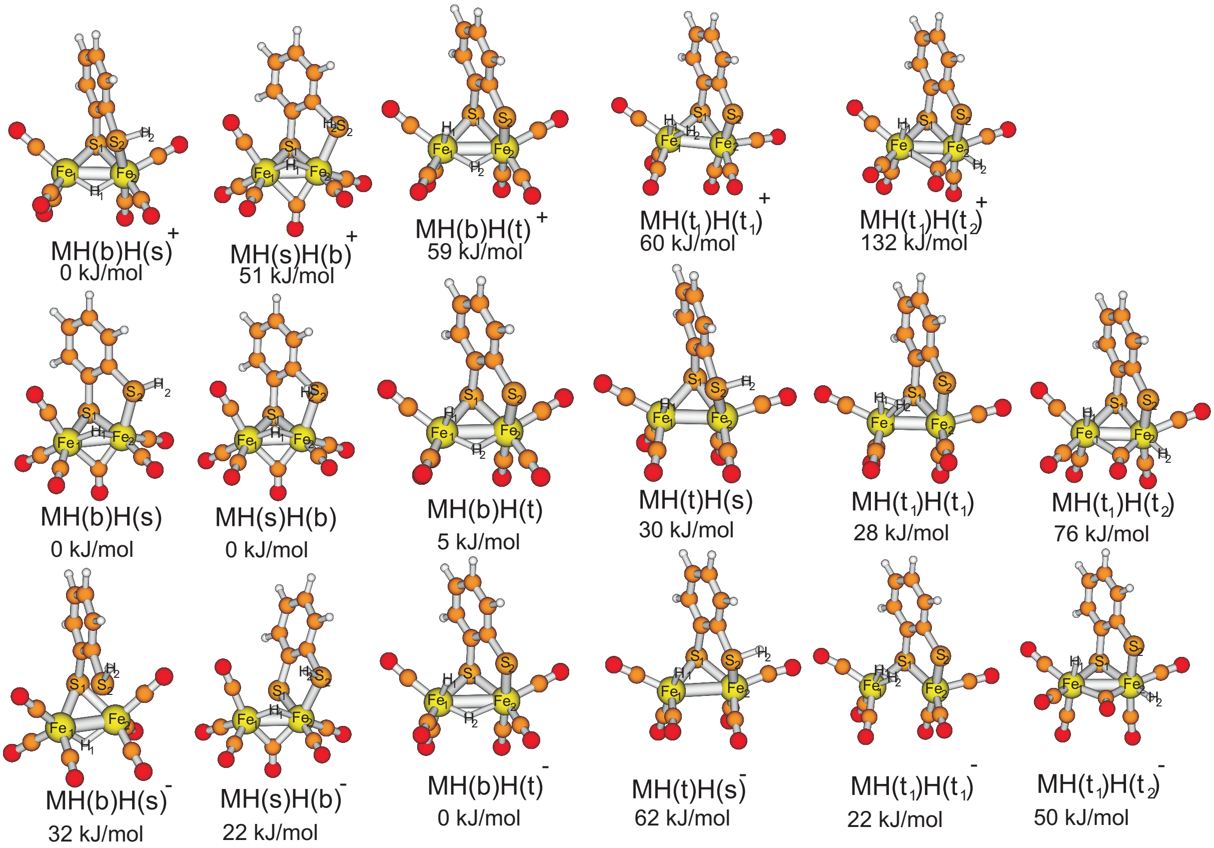
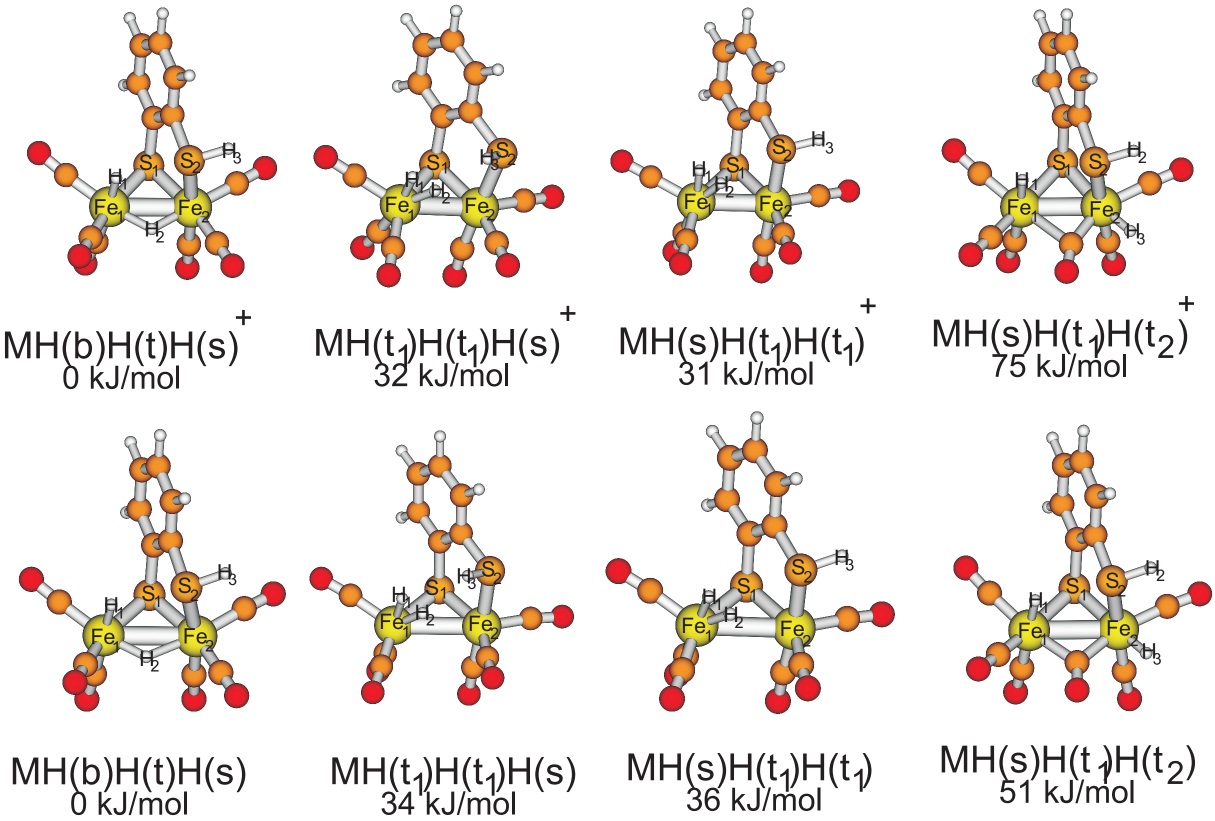


Figure S3: Optimized isomers of the triply protonated complexes with the benzenedithiolato ligand and their relative free energies.



$MH(b)H(t)H(s)^+$ 0 kJ/mol

$MH(t_1)H(t_1)H(s)^+$ 32 kJ/mol

$MH(s)H(t_1)H(t_1)^+$ 31 kJ/mol

$MH(s)H(t_1)H(t_2)^+$ 75 kJ/mol

$MH(b)H(t)H(s)$ 0 kJ/mol

$MH(t_1)H(t_1)H(s)$ 34 kJ/mol

$MH(s)H(t_1)H(t_1)$ 36 kJ/mol

$MH(s)H(t_1)H(t_2)$ 51 kJ/mol