Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

A model theoretical study on ligand exchange reactions of CooA

Toshimasa Ishida[a] and Shigetoshi Aono[b]

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Table S1 Relative stability and the distance between the center iron ion and the axial ligands in the ligand exchange of Cys75 for His77 in the ferric and ferrous states as well as in the protonated/deprotonated state of the sulfur atom in Cys75 for Rr-CooA. The values in normal and italic fonts are at the ONIOM QM/MM level using a larger model and at the QM only level[a]. The values in parentheses are from the EXAFS measurement. [14]

	Multiplicity	ΔE(kcal mol^{-1})	Fe-N(His)	Fe-S(Cys)	Fe-N(Pro)
Fe^{3+}-Cys(S^-)-Met-His	Doublet	0.0	6.34	2.27	2.25
(**R1**)			*6.45*	*2.25*	*2.05*
				(2.25)	(2.19)
Fe^{3+}-His-Met-Cys(S^-)	Doublet	18.4	2.03	4.93	2.16
(**R1'**)		*9.8*	*2.02*	*6.68*	*2.06*
Fe^{2+}-His-Met-Cys(SH)	Singlet	0.0	2.05	8.02	2.19
(**R2**)			*2.04*	*6.68*	*2.05*
			(2.02)		(2.16)
Fe^{2+}-Cys(SH)-Met-His	Singlet	6.7	7.16	2.59	2.12
(**R2'**)		*7.9*	*8.42*	*2.58*	*2.01*
Fe^{3+}-Cys(SH)-Met-His	Doublet	0.0	5.97	2.28	2.21
(**R4**)			*4.94*	*2.29*	*2.11*
Fe^{3+}-His-Met-Cys(SH)	Doublet	-5.6	1.99	8.49	2.13
(**R4'**)		*-11.9*	*1.97*	*10.35*	*2.04*
Fe^{2+} -His-Met-Cys(S^-)	Singlet	0.0	2.04	6.89	2.19
(**R5**)			*2.04*	*7.04*	*2.06*
Fe^{2+}-Cys(S^-)-Met-His	Singlet	3.9	7.98	2.43	2.24

(**R5'**)	*10.8*	*6.81*	*2.46*	*2.07*

[a]Concerning the two models employed, see text in Calculation section.

Table S2 Reaction energies in the exchange of Pro-terminal ligand for gas molecule X (X=CO, NO, and O_2) in Rr-CooA . In the ferric state, Pro-Porphyrin (Fe^{3+})-Cys + X → X -Porphyrin(Fe^{3+})- Cys + Pro. [a,b] In the ferrous state, Pro-Porphyrin (Fe^{2+})-His + X → X -Porphyrin(Fe^{2+})-His + Pro. [a,c] The reaction energy is listed for which the lowest energy gas adduct are generated among possible multiplicities. Energies are in kcal mol^{-1}.

Gas molecule attached (X)	Reactants	
	Ferric [a,b](**R1**) (-Pro-Fe^{3+}-Cys-)	Ferrous [a,c](**R2**) (-Pro-Fe^{2+}-His-)
CO	4.5(8.5)[d]	-10.4 (-5.6) [e]
NO	6.3(10.3) [f] (Dissoc.[g])	-4.5 (0.3) [d]
O_2	-20.7(-17.7) [d] (Dissoc.[g])	9.5 (14.3) [f]

[a] The proline (Pro) terminal is modeled by Pro2 and a part of Pro3, 1-(1-pyrrrolidine)-1'-(3-pyrrolidine)-methanone, in the larger model or pyrrolidine in the smaller model (in parentheses).

[b] Cysteine(Cys) is modeled by thiomethy anion (CH_3S^-)

[c] Histidine (His) is modeled by imidazole.

[d] The lowest energy gas-adduct is in the doublet.

[e] The lowest energy gas-adduct is in the singlet.

[f] The lowest energy gas-adduct is in the triplet.

[g] The bond between the iron and the gas molecule is dissociated.

Table S3 Reaction energies in the exchange of NH_2-Ala-terminal ligand for gas molecule X (X=CO, NO, and O_2) in Ch-CooA : NH_2-Ala-Porphyrin (Fe^{3+}/ Fe^{2+})-His + X → X -Porphyrin(Fe^{3+}/ Fe^{2+})-His + Ala [a,b,c] The reaction energy is listed for which the lowest energy gas adduct are generated among possible multiplicities. Energies are in kcal mol^{-1}.

Gas molecule attached (X)	Reactants	
	Ferric (**C1**) [a,b] (-Ala-NH_2-Fe^{3+}- His-)	Ferrous (**C2**) [a,b] (-Ala-NH_2-Fe^{2+}-His-)
CO	11.9(10.1) [c]	-8.9 (-2.7) [d]
NO	16.1(14.4) [d]	-2.9 (3.3) [c]
O_2	24.0(22.2) [e]	10.8 (17.2) [f]

[a] The alanine (Ala) terminal is modeled by Ala2 and a part of Thr3, *N*-(2-propanal)-1-aminopropaneamide, in the larger model or ethyl amine in the smaller model (in parentheses). Note that amino-group in alanine is coordinated to the ferric/ferrous iron atom.

[b] Histidine (His) is modeled by imidazole.

[c] The lowest energy product is in the doublet.

[d] The lowest energy product is in the singlet.

[e] The lowest energy product is in the quartet.

[f] The lowest energy product is in the triplet.