## Supporting Information

for

# Geometric Preferences in Iron(II) and Zinc(II) Model Complexes of Peptide Deformylase 

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General procedures. Synthesis of complex 1 was carried out under inert atmosphere using dry box and Schlenk techniques. No special precautions were taken for the syntheses of complexes 2 and 3. $\mathrm{Py}_{2} \mathrm{SH}^{1}$ and $\mathrm{Fe}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}^{2}$ were prepared according to literature procedures. For the synthesis of complex 1, MeOH was dried by refluxing over $\mathrm{CaH}_{2}$ for 18 hours and then distilled. Diethyl ether was distilled under $\mathrm{N}_{2}$ from sodium/benzophenone. Traces of oxygen were removed from these solvents by 3 cycles of freeze-pump-thaw. Other commercially available reagents were used as received. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra in $\mathrm{CD}_{3} \mathrm{OD}$ or $\mathrm{CD}_{3} \mathrm{CN}$ were recorded on a Varian Unity Plus 400 spectrometer ( 400 MHz ) at ambient probe temperature with the solvent peak as the internal reference. IR spectra were recorded on a Bruker Vector 22 FTIR spectrophotometer as KBr disks or as a solution in acetonitrile. Elemental analyses were recorded at Atlantic Microlab, Inc., Norcross, GA.

X-ray crystallography. Diffraction intensity data were collected at 100 K for $\mathbf{1}$ and 110 K for $\mathbf{2}$ and $\mathbf{3}$ on an Oxford Diffraction Xcalibur3 diffractometer equipped with a graphite monochromator and an Enhanced (Mo) X-ray Source ( $\square=0.71073 \AA$ ) operated at 2 kW power ( $50 \mathrm{kV}, 40 \mathrm{~mA}$ ). The detector was placed at a distance of 50 mm from the crystal. The structures were solved by the direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on $\mathrm{F}^{2}$. Faceindexed absorption corrections were applied to the data for $\mathbf{1}-\mathbf{3}$. Hydrogen atoms were refined in idealized positions riding on the attached atom, with appropriate constants times the $\mathrm{U}(\mathrm{eq})$ of the attached atom. The H atoms in $\mathbf{1}$ were treated as idealized contributions. The H atoms in $\mathbf{2}$ and $\mathbf{3}$ were found on the F-maps and refined with isotropic thermal parameters. All software and sources of scattering factors are contained in the SHELXTL (6.10) program package (G.Sheldrick, Bruker XRD, Madison, WI). Analysis of the data showed only negligible decay.

Computational Details. All our DFT calculations are carried out using B3LYP hybrid exchange-correlation functional ${ }^{3,4}$ and $6-311 \mathrm{G}^{*}$ basis set with Gaussian 03 software. ${ }^{5}$ The X-ray structures determined for $\left(\mathrm{Py}_{2} \mathrm{~S}\right) \mathrm{Fe}\left(\mathrm{O}_{2} \mathrm{CH}\right)$ and $(\mathrm{PATH}) \mathrm{Zn}\left(\mathrm{O}_{2} \mathrm{CH}\right)^{6}$ are used as the starting structures for optimization of both the Fe and Zn species. For the Fe species, the geometry optimization was performed for spin states from singlet up to quintet to determine the ground spin state, and the spin quintet turns out to be the ground state for both cases. Therefore, all our results for the Fe species correspond to the spin quintet.

Synthesis of $\left[\left(\mathbf{P y}_{2} \mathbf{S}\right) \mathbf{F e}\left(\mathbf{O}_{\mathbf{2}} \mathbf{C H}\right)\right]$ (1). To a solution of $\mathrm{Py}_{2} \mathrm{SH}(0.126 \mathrm{~g}, 0.40 \mathrm{mmol})$ in dry $\mathrm{MeOH}(4 \mathrm{~mL})$ was added $\mathrm{NaOH}(0.018 \mathrm{~g}, 0.44 \mathrm{mmol})$ in dry $\mathrm{MeOH}(5 \mathrm{~mL})$, and stirred
for one hour. The $\mathrm{Py}_{2} \mathrm{SNa}^{+}$solution was then added to a suspension of $\mathrm{Fe}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ $(0.08 \mathrm{~g}, 0.44 \mathrm{mmol})$ in dry $\mathrm{MeOH}(5 \mathrm{~mL})$ and the reaction mixture was stirred for 18 h , affording a clear yellow solution. Methanol was removed under vacuum to give an orange solid. The orange solid was dissolved in anhydrous toluene and filtered through celite. The resulting clear orange solution was set for $\mathrm{Et}_{2} \mathrm{O}$ diffusion. Orange crystals of $\mathbf{1}$ were obtained after 14 days. Yield: $0.012 \mathrm{~g}, 7 \%$. Anal. Calc. for $\mathrm{C}_{19} \mathrm{H}_{25} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{SFe}$ : C, 54.94; H, 6.07; N, 10.12. Found: C, 54.82; H, 5.96; N, 10.02. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{3} \mathrm{CN}, \mathrm{ppm}\right): \square$ 77.8, 41.0, 34.7, 28.9, -4.9, -16.8, -24.4. IR (KBr, $\left.\mathrm{cm}^{-1}\right)$ : $\square 3063,3022,2953,2917,2854$, $2784,1630,1605,1567,1485,1443,1378,1356,1303,1161,1142,1099,1079,1063$, 1019. IR $\left(\mathrm{CH}_{3} \mathrm{CN}, \mathrm{cm}^{-1}\right): \square 2969,2938,2858,1625,1608,1592,1570,1475,1448,1359$, 1315, 1108, 1087, 1021, 993.

Synthesis of $\left[\left(\mathbf{P y}_{2} \mathbf{S}\right)(\mathbf{Z n})_{\mathbf{2}}\left(\mathbf{O}_{\mathbf{2}} \mathbf{C H}\right)_{3}\right]$ (2). To a solution of $\mathrm{Py}{ }_{2} \mathrm{SH}(0.089 \mathrm{~g}, 0.28 \mathrm{mmol})$ in $\mathrm{MeOH}(5 \mathrm{~mL})$ was added $\mathrm{NaOH}(0.012 \mathrm{~g}, 0.31 \mathrm{mmol})$ in $\mathrm{MeOH}(5 \mathrm{~mL})$, and stirred under argon for 90 minutes. An amount of $\mathrm{Zn}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}(0.059 \mathrm{~g}, 0.31 \mathrm{mmol})$ was dissolved in $\mathrm{MeOH}(5 \mathrm{~mL}$ ) and stirred under argon for 15 minutes. The methanolic solution of $\mathrm{Py}_{2} \mathrm{SNa}^{+}$was added dropwise to the solution of $\mathrm{Zn}\left(\mathrm{O}_{2} \mathrm{CH}\right)_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ and the reaction mixture was stirred for 18 h under argon to give a clear colorless solution. Methanol was removed under reduced pressure to afford a white solid. This white solid was dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and the solution was filtered and set for $\mathrm{Et}_{2} \mathrm{O}$ diffusion. Colorless crystals of $\mathbf{2}$ were obtained after 10 days. Yield: 0.026 g, 29\%. Anal. Calc. for $\mathrm{C}_{21} \mathrm{H}_{27} \mathrm{~N}_{3} \mathrm{O}_{6} \mathrm{SZn}_{2}$ : C, 43.46; H, 4.69; N, 7.24. Found: C, 43.45; H, 4.70; N, 7.26. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{3} \mathrm{OD}, \mathrm{ppm}\right): \square 1.28\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}\right), 2.81\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 2.88\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 3.1(\mathrm{~m}, 4 \mathrm{H}$, $\left.\mathrm{CH}_{2}\right), 3.26\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{CH}_{2}\right), 7.61\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{H}_{\square}\right.$ and $\left.\mathrm{H}_{\square}\right), 8.12\left(\mathrm{dt}, 2 \mathrm{H}, \mathrm{H}_{\square}\right), 8.38\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{O}_{2} \mathrm{CH}\right)$,
8.76 (d, 2H, $\mathrm{H}_{\square}$ ). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\square 33.9,34.3,58.4,71.9,125.2,127.3$, 143.2, 151.2, 162.7, 170.6. IR (KBr, $\left.\mathrm{cm}^{-1}\right)$ : $\square 2961,2922,2864,2816,1649,1633,1614$, $1588,1569,1489,1448,1378,1354,1342,1322,1276,1162,1143,1112,1079,1065$, 1028, 774, 651, 595.

Synthesis of $\left[\left(\mathbf{P y}_{2} \mathbf{S}\right)_{\mathbf{2}}(\mathbf{Z n})_{\mathbf{3}}\left(\mathbf{O}_{\mathbf{2}} \mathbf{C H}\right)_{\mathbf{2}}\left(\mathbf{B F}_{4}\right)_{2}\right]$ (3). To a solution of $\mathrm{Py}_{2} \mathrm{SH}(0.064 \mathrm{~g}, 0.20$ $\mathrm{mmol})$ in $\mathrm{MeOH}(5 \mathrm{~mL})$ was added $\mathrm{NaOH}(0.009 \mathrm{~g}, 0.22 \mathrm{mmol})$ in $\mathrm{MeOH}(5 \mathrm{~mL})$, and stirred for one hour. An amount of $\mathrm{Zn}\left(\mathrm{BF}_{4}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}(0.053 \mathrm{~g}, 0.22 \mathrm{mmol})$ was dissolved in $\mathrm{MeOH}(5 \mathrm{~mL})$ and stirred for 15 minutes. The methanolic solution of $\mathrm{Py}_{2} \mathrm{~S} \mathrm{Na}^{+}$was added dropwise to the solution of $\mathrm{Zn}\left(\mathrm{BF}_{4}\right)_{2} \cdot \mathrm{H}_{2} \mathrm{O}$ and the reaction mixture was stirred for 18 h . A solution of $\mathrm{NaO}_{2} \mathrm{CH}(0.015 \mathrm{~g}, 0.22 \mathrm{mmol})$ in $\mathrm{MeOH}(5 \mathrm{~mL})$ was added to the reaction mixture and stirred for 18 hours. Methanol was removed under reduced pressure to give a white solid, which was re-dissolved in a minimum amount of MeOH and set for $\mathrm{Et}_{2} \mathrm{O}$ diffusion. Colorless crystals of $\mathbf{3}$ were obtained after 20 days. Yield: $0.027 \mathrm{~g}, 24 \%$. Anal. Calc. for $\mathrm{C}_{39} \mathrm{H}_{54} \mathrm{~N}_{6} \mathrm{O}_{5} \mathrm{~S}_{2} \mathrm{Zn}_{3} \mathrm{~B}_{2} \mathrm{~F}_{8}\left(3 \cdot \mathrm{CH}_{3} \mathrm{OH}\right)$ : C, 41.79 ; H, 4.86; $\mathrm{N}, 7.50$. Found: C, 41.07; H, 4.56; N, 7.59. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{3} \mathrm{OD}, \mathrm{ppm}\right): 1.21\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{CH}_{3}\right), 2.79(\mathrm{~s}, 4 \mathrm{H}$, $\left.\mathrm{CH}_{2}\right), 2.91\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right), 3.09\left(\mathrm{~m}, 8 \mathrm{H}, \mathrm{CH}_{2}\right), 3.30\left(\mathrm{CH}_{2}\right.$, overlapped with MeOH solvent peak), $7.64\left(\mathrm{~m}, 8 \mathrm{H}, \mathrm{H}_{\square}\right.$ and $\left.\mathrm{H}_{\square}\right), 8.14\left(\mathrm{dt}, 4 \mathrm{H}, \mathrm{H}_{\square}\right), 8.41\left(\mathrm{~s}, 2 \mathrm{H}, O_{2} C \mathrm{H}\right), 8.65\left(\mathrm{~d}, 4 \mathrm{H}, \mathrm{H}_{\square}\right)$. IR (KBr, $\left.\mathrm{cm}^{-1}\right)$ : $\square 2966,2860,1631,1611,1591,1568,1489,1448,1350,1320,1083$, 772, 651, 597, 534, 522, 473, 420.


Figure S1. Thermal ellipsoid plot of $\mathbf{2}$ with $40 \%$ probability. Hydrogen atoms are omitted for clarity.


Figure S2. Thermal ellipsoid plot of $\mathbf{3}$ with $40 \%$ probability. Hydrogen atoms and $\mathrm{BF}_{4}{ }^{-}$ units are omitted for clarity.


Figure S3. Potential energy surface of $\left(\mathrm{Py}_{2} \mathrm{~S}\right) \mathrm{M}^{2+}\left(\mathrm{O}_{2} \mathrm{CH}\right)(\mathrm{M}=\mathrm{Fe}, \mathrm{Zn})$ along the $\mathrm{M}-\mathrm{O}(2)$ bond from B3LYP/6-311G* calculations. For each point, geometry optimization has been carried out with the $\mathrm{M}-\mathrm{O}(2)$ bond length fixed.


Figure S4. Geometry optimized structure of $\left(\mathrm{Py}_{2} \mathrm{~S}\right) \mathrm{Fe}\left(\mathrm{O}_{2} \mathrm{CH}\right)$ (isomer a) from B3LYP/6$311 \mathrm{G}^{*}$ calculations.


Figure S5. Geometry optimized structure of $\left(\mathrm{Py}_{2} \mathrm{~S}\right) \mathrm{Zn}\left(\mathrm{O}_{2} \mathrm{CH}\right)$ from B3LYP/6-311G* calculations.


Figure S6. Geometry optimized structure of (PATH) $\mathrm{Zn}\left(\mathrm{O}_{2} \mathrm{CH}\right)$ from B3LYP/6-311G* calculations.

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