Supplementary Information for…

Fluxionality in a paramagnetic seven-coordinate iron(II) complex: a variable temperature, two-dimensional NMR and DFT study

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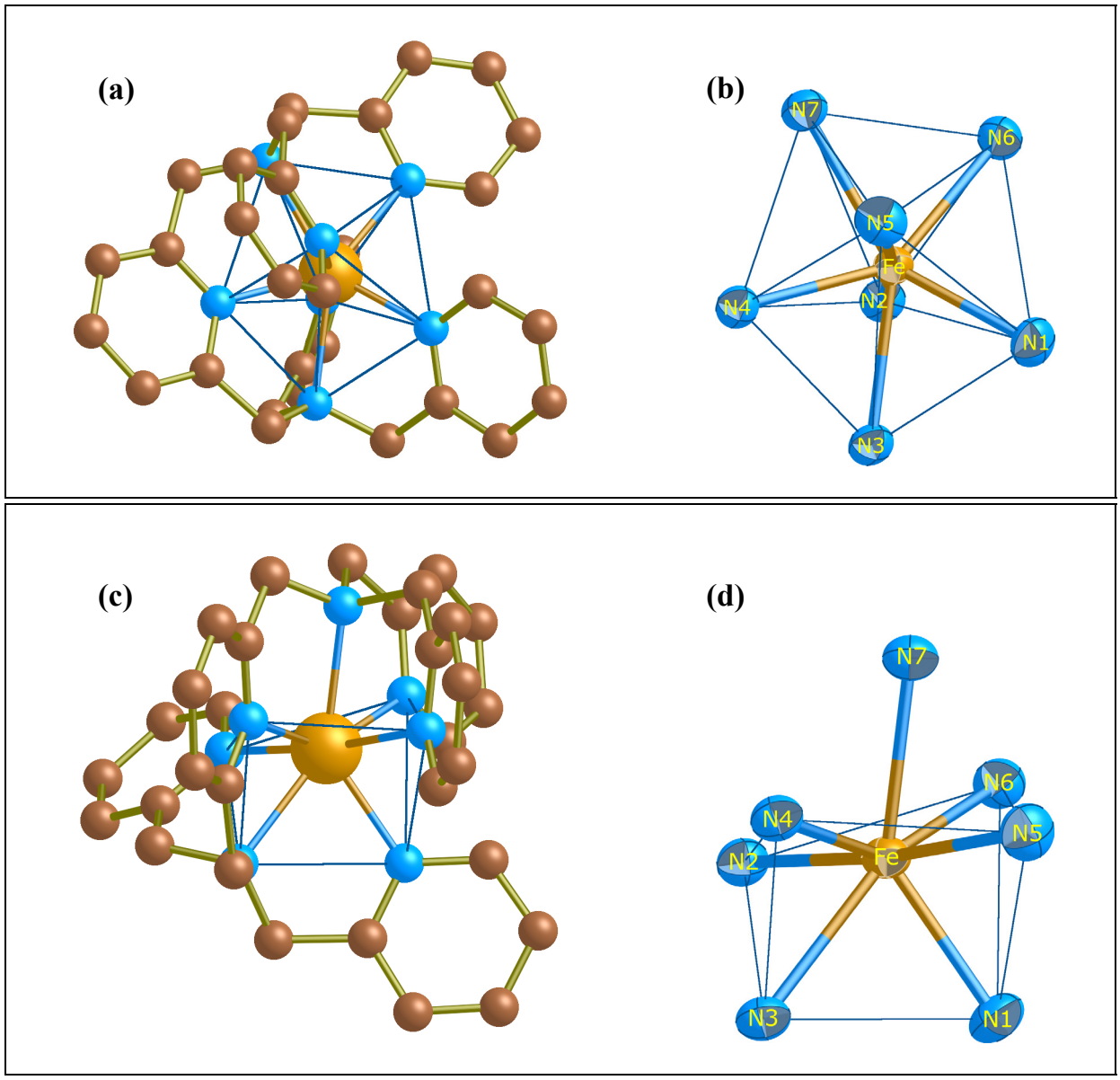


Figure 1S. Views of the $[Fe(L)]^{2+}$ cation from the X-ray crystal structure of $[Fe(L)](ClO_4)_2$ emphasizing alternative descriptions of the coordination geometry as pentagonal bipyramidal (a), (b) or face-capped trigonal prismatic (c), (d). In the face-capped trigonal prismatic description, amine N7 is in the capping position and the structure is asymmetric (C_s symmetry). In the pentagonal bipyramidal description, the complex ion has pseudo-C_2 symmetry, which accords with the NMR spectra, and pyridyls N1 and N6 are equatorial (in the pentagonal plane) whereas pyridyls N2 and N5 are axial (bound below and above the pentagonal plane). (a) and (c) show ball-and-stick views of the cation with H-atoms omitted for clarity, and (b) and (d) show labelled 30% thermal elipsoids for the iron and the N-donor atoms.

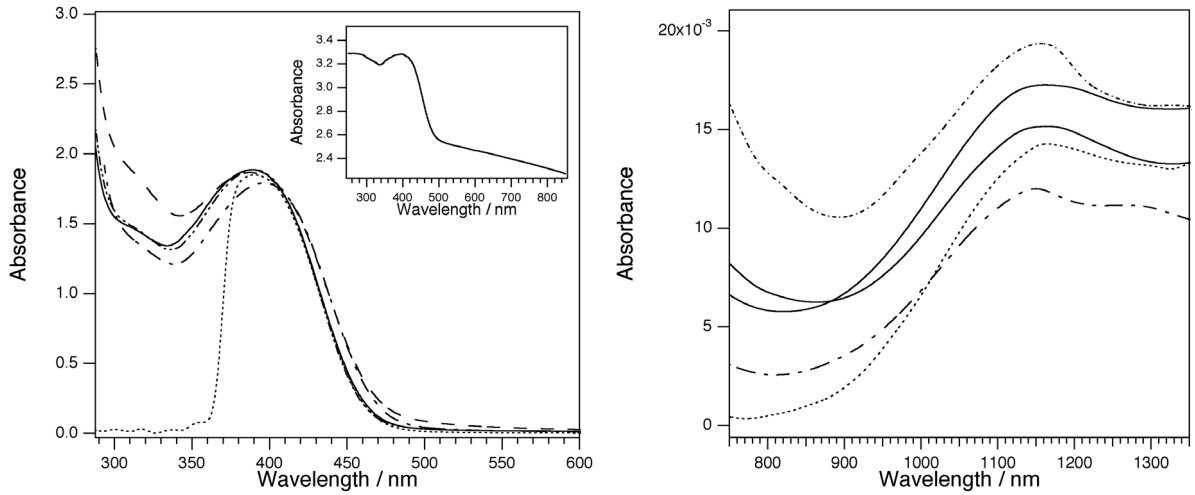


Figure 2S. UV-Vis-NIR spectra of $[Fe(L)](ClO_4)_2$ in the solid-state (inset) and in acetonitrile (—), dimethylformamide (---), dichloromethane (-···-) and nitromethane (···) solution (that the absorbance drops to zero below ~370 nm in the nitromethane solution is an instrumental artifact resulting from improper compensation for the strong solvent absorbance in this region).

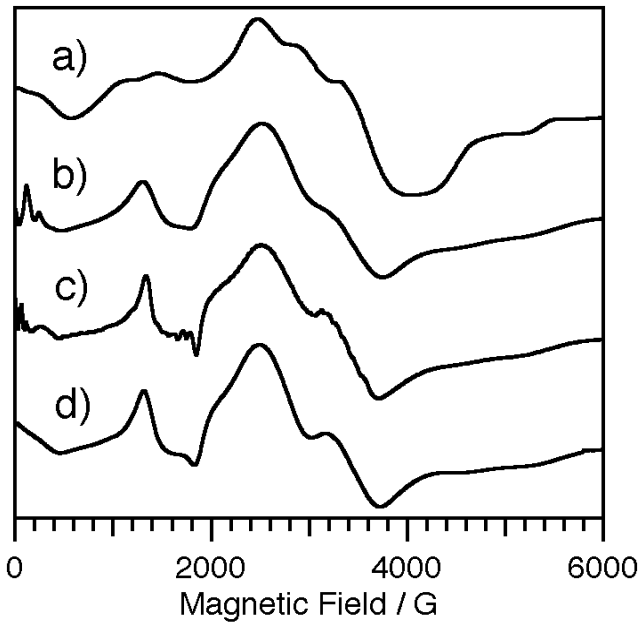


Figure 3S. X-band EPR spectra of $[Mn(L)](ClO_4)_2$ at 77 K in: (a) the solid-state; (b) acetonitrile solution; (c) dimethylformamide solution; (d) dichloromethane solution.

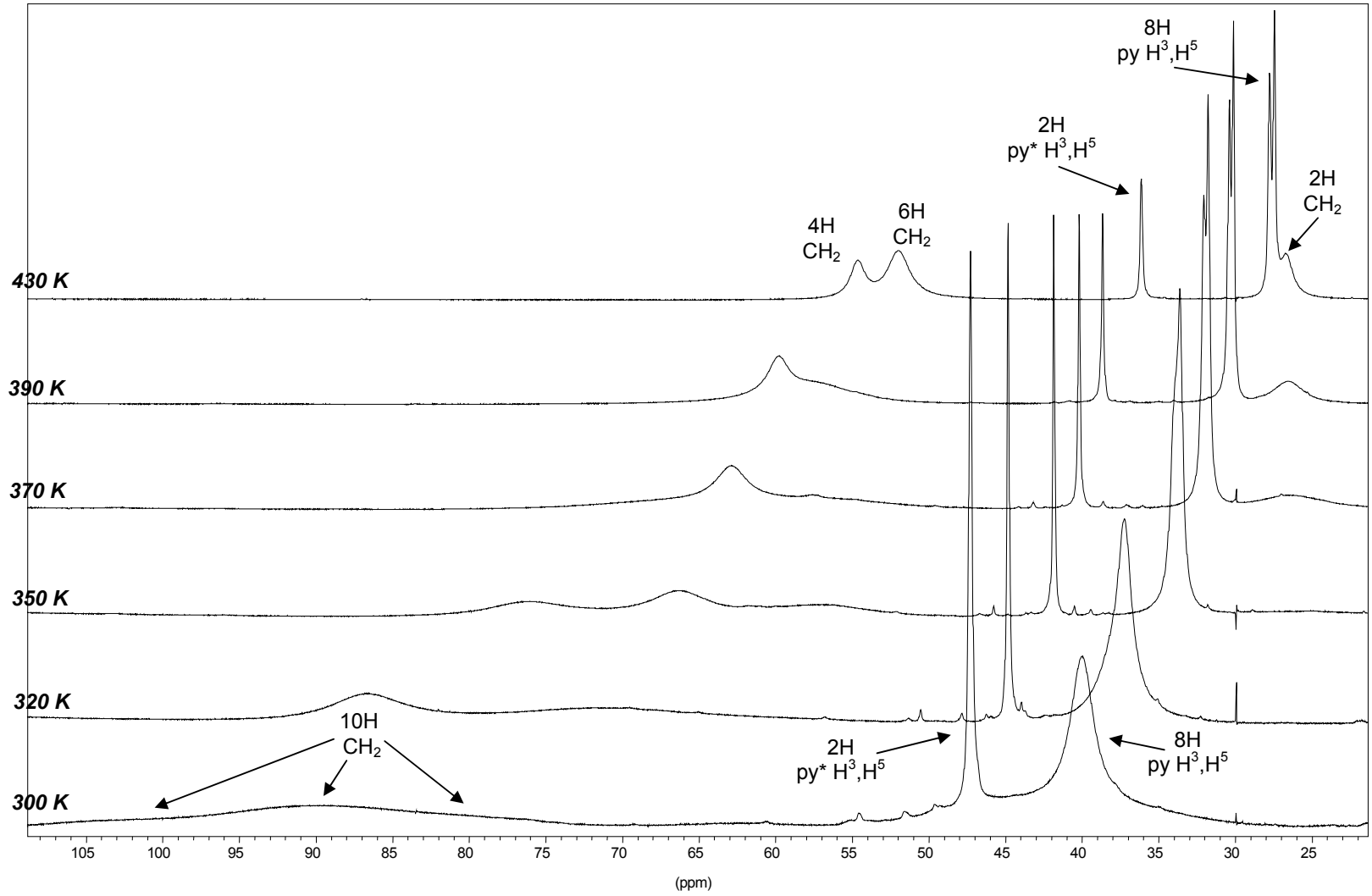


Figure 4S(a). 300 MHz variable temperature ^{1}H NMR spectra of [Fe(L)](ClO$_4$)$_2$ in d_6-dmso (δ +109 to +22).

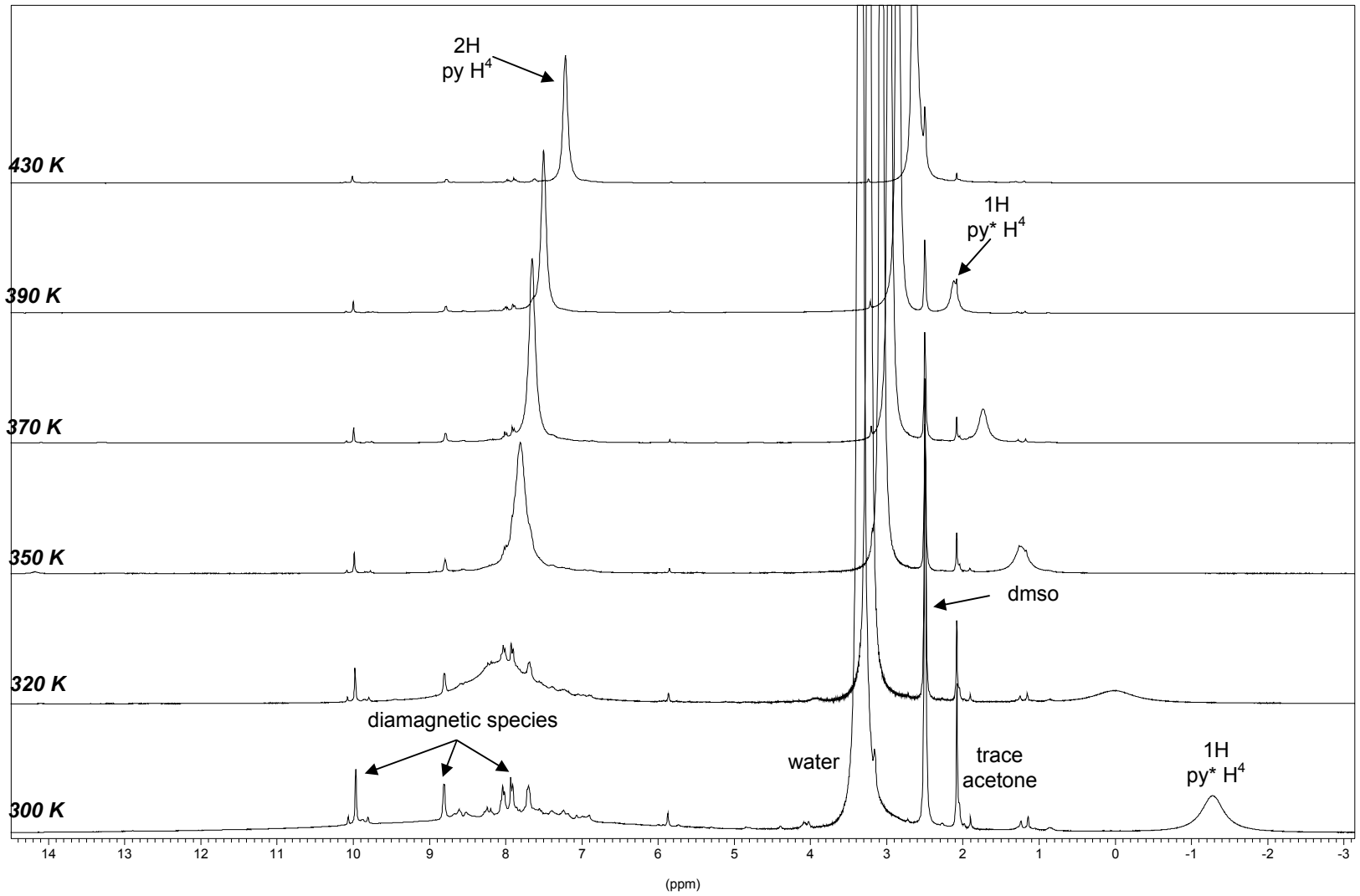


Figure 4S(b). 300 MHz variable temperature ^{1}H NMR spectra of [Fe(L)]$(ClO_4)_2$ in d_6-dmso (δ +14 to –3); sharp peaks from diamagnetic solvent and impurities are indicated.

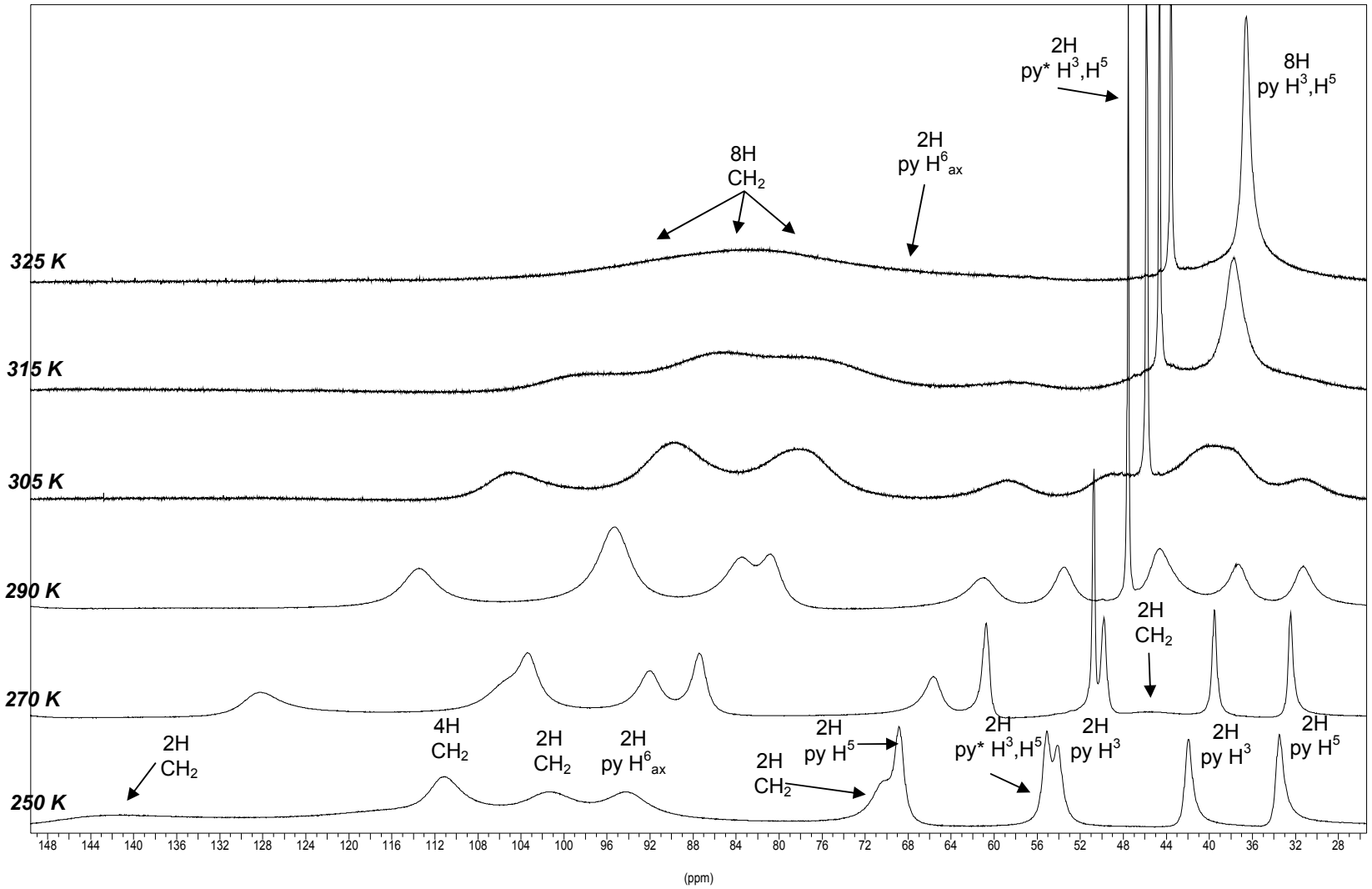


Figure 5S(a). 300 MHz variable temperature ^{1}H NMR spectra of $[Fe(L)](ClO_4)_2$ in CD_3OD (δ +150 to +25).

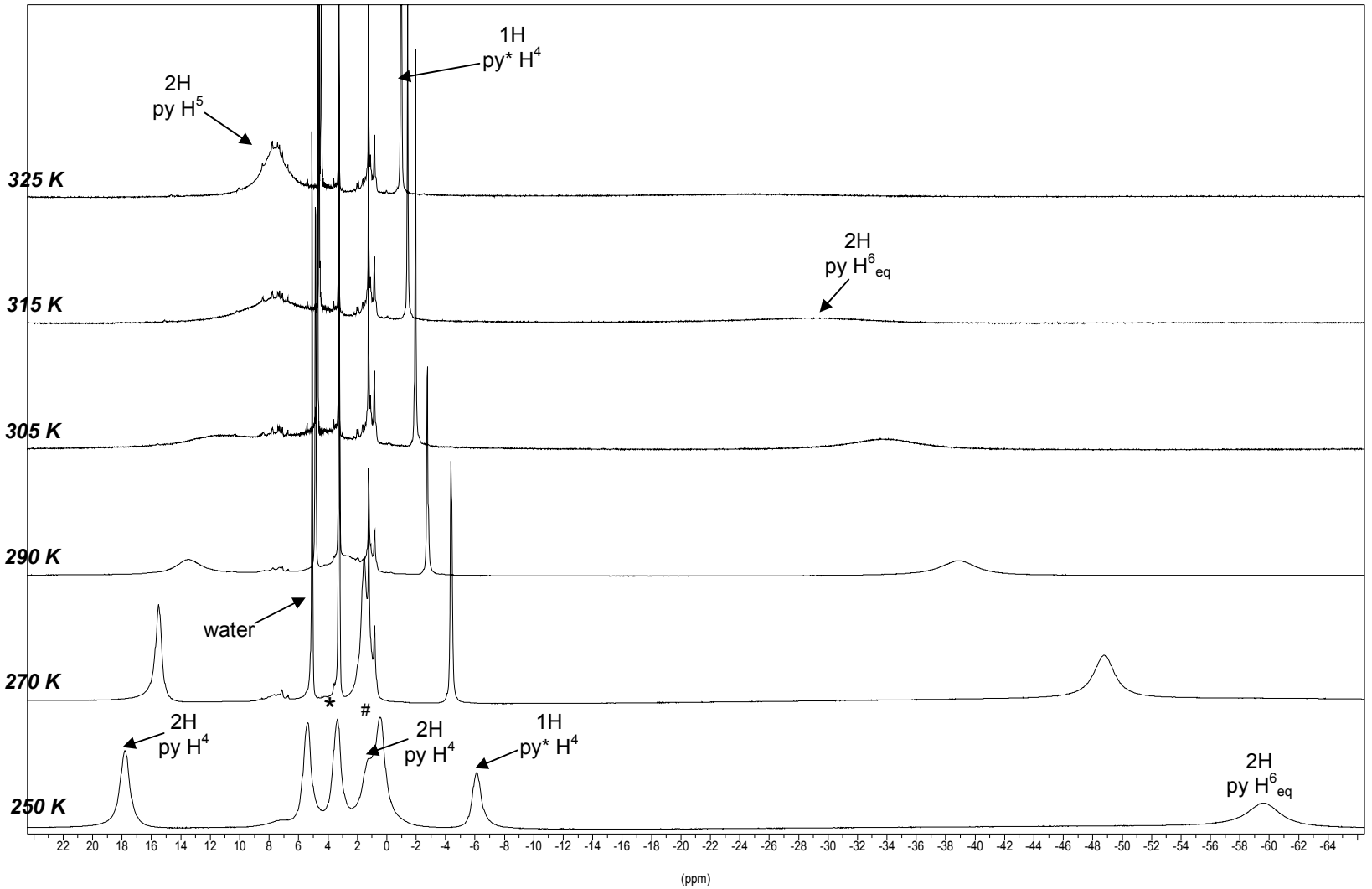


Figure 5S(b): 300 MHz variable temperature ^{1}H NMR spectra of $[Fe(L)](ClO_4)_2$ in CD_3OD (δ 24 to –66). ⁎ protio-methanol, # protio-water.

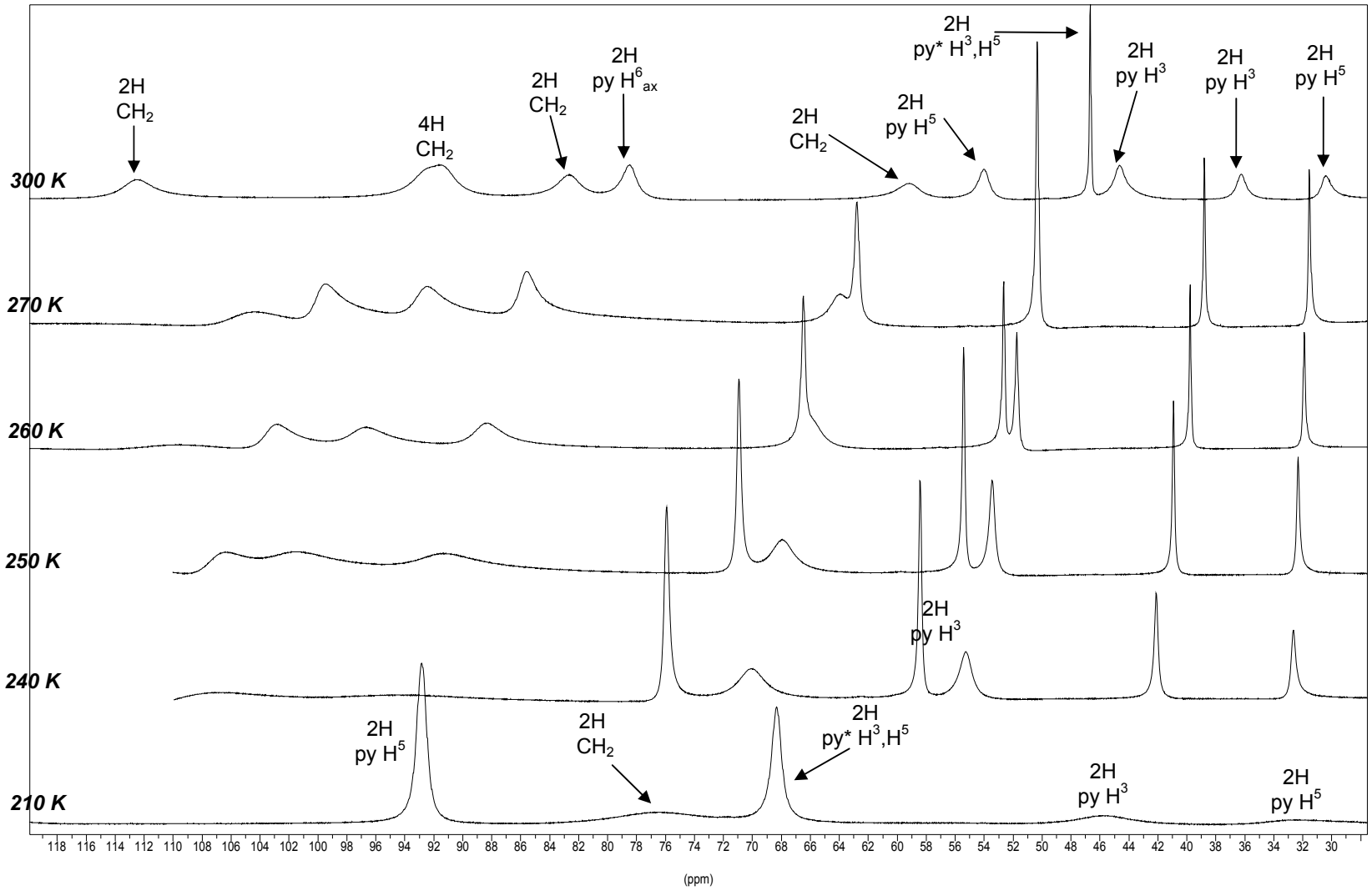


Figure 6S(a). 300 MHz variable temperature ^{1}H NMR spectra of $[Fe(L)](ClO_4)_2$ in CD_2Cl_2 (δ +120 to +28).

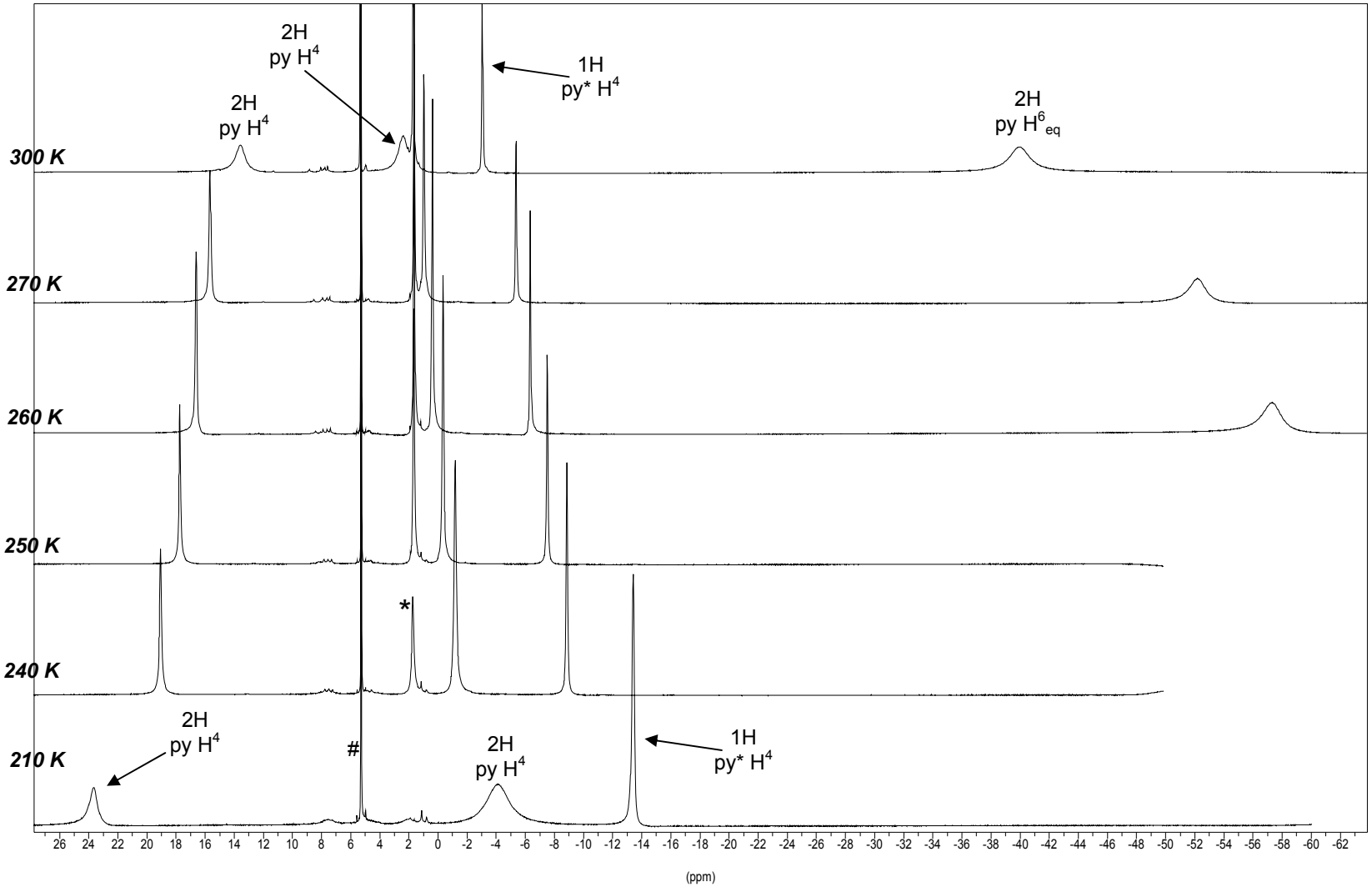


Figure 6S(b): 300 MHz variable temperature ^{1}H NMR spectra of $[Fe(L)](ClO_4)_2$ in CD_2Cl_2 (δ +28 to –64). **#** protio-dichloromethane, $*$ protio-water.

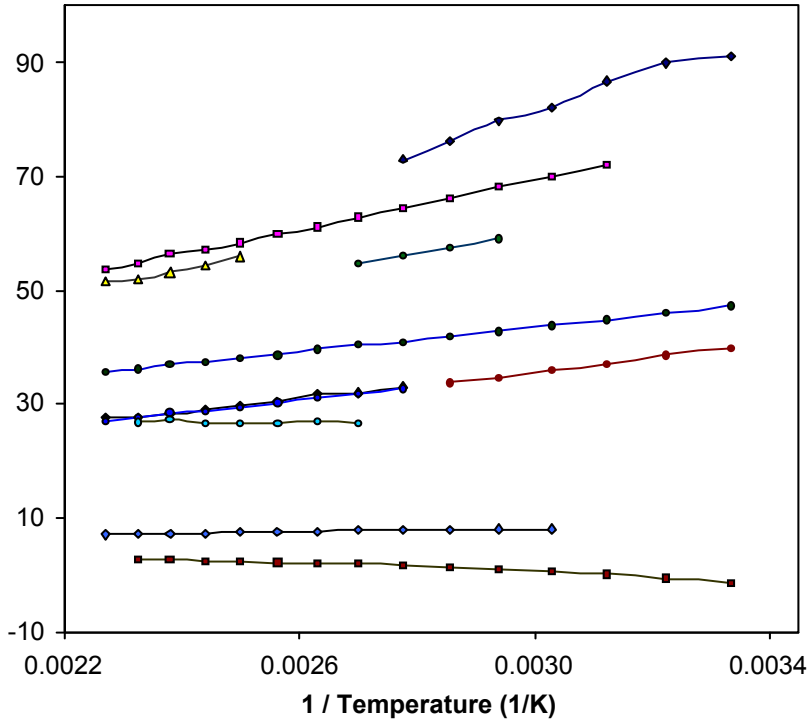


Figure 7S. Plot of chemical shift versus inverse temperature for the signals in ^{1}H NMR spectra of [Fe(L)]$(ClO_4)_2$ in d_6-dmso.

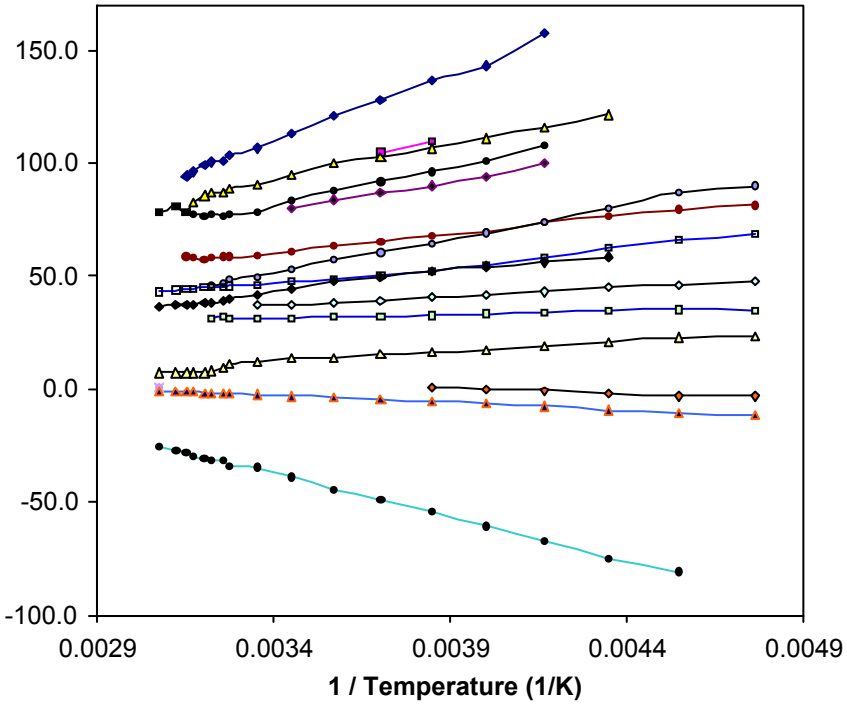


Figure 8S. Plot of chemical shift versus inverse temperature for the signals in the ^{1}H NMR spectra of [Fe(L)]$(ClO_4)_2$ in CD_3OD.

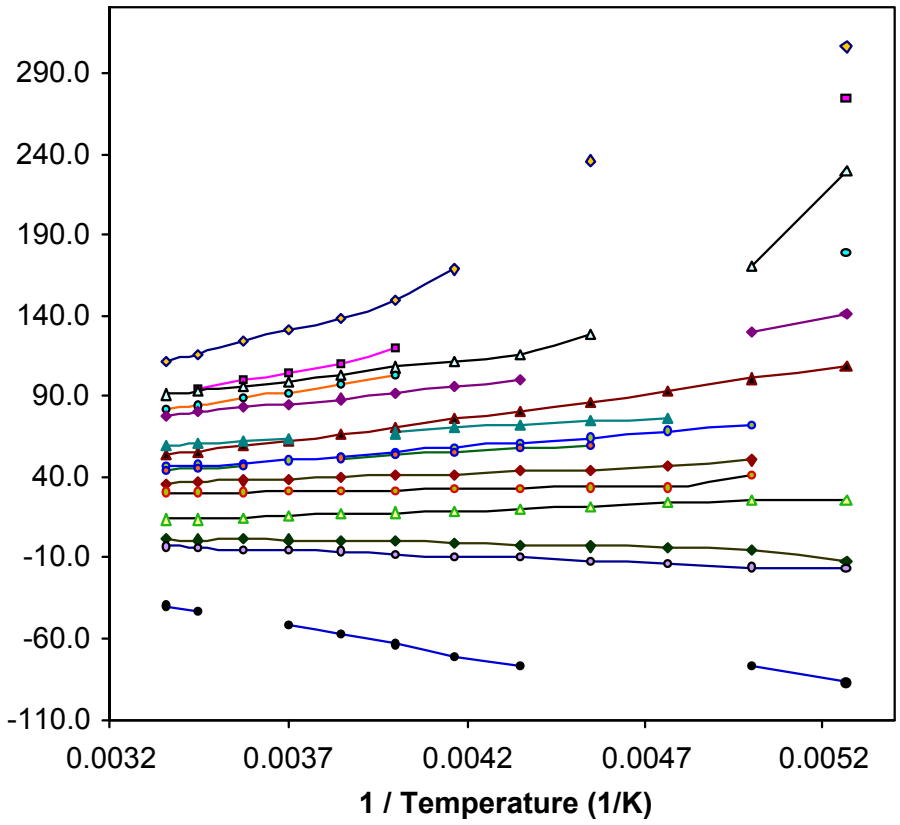


Figure 9S. Plot of chemical shift versus inverse temperature for the signals in the ^{1}H NMR spectra of $[Fe(L)](ClO_4)_2$ in CD_2Cl_2.

Table 1S: ^{1}H chemical shifts and T_1 values for [Fe(L)]$(ClO_4)_2$ in d_6-dmso at 298 K. Peaks for two CH_2 protons, two H^6_{ax} protons and two H^4 protons (overlapped with impurity) were not observed in the spectra at 298 K.

Proton assignment	^{1}H chemical shift (ppm)	T_1 relaxation times (msec)
CH_2 (2H)	102.7	0.5
CH_2 (6H)	89.5	0.3
CH_2 (2H)	63.2	0.5
$H^{3,5}$(py*) (2H)	47.3	7.6
$H^{3.5}$(py) (8H)	40.0	7.7
H^4(py) (2H)	8.5	17
H^4(py*) (1H)	-1.3	9.5
H^6_{eq}(py) (2H)	-30.0	0.5

Table 2S: ^{1}H chemical shifts and respective T_1 values for protons of [Fe(L)]$(ClO_4)_2$ in CD_3OD at 298 K. Note that two CH_2 protons are not listed as these protons do not display a peak in CD_3OD at 298 K.

Assignment	Chemical shift (ppm)	T_1 relaxation times (msec)
CH_2 (2H)	106.8	0.1
CH_2 (4H)	91.1	0.3
H^6_{ax}(py) (2H) & CH_2 (2H) overlapped	78.7	0.1
CH_2 (2H)	59.3	0.7
H^5(py) (2H)	50.3	7.1
$H^{3,5}$(py*) (2H)	46.2	4.0
H^3(py) (2H)	41.9	4.1
H^3(py) (2H)	38.0	4.9
H^5(py) (2H)	31.3	3.3
H^4(py) (2H)	11.9	2.5
H^4(py) (2H)	3.0	
H^4(py*) (1H)	-2.2	10.2
H^6_{eq}(py) (2H)	-34.8	1.4

Table 3S. Intramolecular non-bond Fe…H distances within the $[Fe(L)]^{2+}$ cation.

Distance / Å			
Fe…H (outer PY)			
axial		*equatorial*	
Fe…H^6(py)	3.47	Fe…H^6(py)	3.21
Fe…H^5(py)	5.42	Fe…H^5(py)	5.25
Fe…H^4(py)	6.11	Fe…H^4(py)	5.98
Fe…H^3(py)	5.22	Fe…H^3(py)	5.17
Fe…H (central PY)			
Fe…H^5(py*)	5.11	Fe…H^3(py*)	5.10
Fe…H^4(py*)	5.66		
Fe…H (methylene)			
Fe…H^a	4.01	Fe…H^b	3.42
Fe…H^c	4.05	Fe…H^d	3.38
Fe…H^e	4.00	Fe…H^f	3.37

Table 4S*:* ^{1}H and ^{13}C chemical shifts (± 0.5 ppm) and ^{1}H–^{13}C coupling constants (± 2 Hz) of protons and carbons in $[Fe(L)](ClO_4)_2$ in d_6-dmso at 410 K that could be definitely determined from ^{1}H and ^{1}H–^{13}C HMQC NMR spectra. The last column lists peaks to which the peaks in the second column show a three bond ^{1}H–^{1}H correlation, as measured by ^{1}H–^{1}H COSY and ^{1}H–^{1}H TOCSY experiments. In d_6-dmso at 410 K, two CH_2 protons and all four H^6 protons could not be definitely assigned.

Proton Assignment	^{1}H Chemical shift (ppm)	^{13}C Chemical shift (ppm)	^{1}H–^{13}C Coupling constants (Hz)	Three-bond ^{1}H–^{1}H correlation to peak (ppm)
CH_2 (4H)	56.8			
CH_2 (6H)	54.3			
$H^{3,5}$(py*) (2H)	37.1	352.4	174	2.4
$H^{3\text{ or }5}$(py) (4H)	28.9	281.7	174	7.3
$H^{3\text{ or }5}$(py) (4H)	28.6	335.7	162	7.3
CH_2 (2H)	26.5			
H^4(py) (4H)	7.3	143.0	168	28.9 and 28.6
H^4(py*) (1H)	2.4	164.2	186	37.1

***Table 5S**:* ^{1}H and ^{13}C chemical shifts (± 0.5 ppm) and $^{1}H–^{13}C$ coupling constants (± 3 Hz) of protons and carbons for $[Fe(L)](ClO_4)_2$, in CD_3OD at 268 K that could be definitely assigned from an $^{1}H–^{13}C$ HMQC experiment.

Proton Assignment	^{1}H chemical shift (ppm)	^{13}C chemical shift (ppm)	^{1}H-^{13}C coupling constants (Hz)
$H^{3,5}$(py*) (2H)	50.5	263.3	175
H^{4}(py) (2H)	49.5	259.6	
H^{4}(py) (2H)	39.4	256.3	185
H^{3}(py) (2H)	15.4	195.8	185
H^{4}(py*) (1H)	-4.2	193.8	175

Calculation of thermodynamic parameters from NMR exchange experiments

***Table 6S**:* Exchange rates, 1/T, ln(k/T) values and evaluated thermodynamic parameters calculated from EXSY spectra at various temperatures with specified mixing times.

Temperature (K)	Mixing time (μs)	Rate (s^{-1})	1/T	Ln(k/T)
296.88	170	625.2	0.0033557	0.74472799
307.2	80	1422.0	0.0032468	1.53232413
311.9	50	2190.0	0.0031949	1.94897214
273.8	800	103.8	0.0035971	-0.9699801
250.5	8000	10.3	0.003876	-3.194865

Rates were calculated by comparing diagonal and cross peaks for the same pair of exchanging protons in all EXSY spectra, specifically the pair at δ 54 and δ 30 at 297 K as these were least overlapped. Mixing times were selected to produce cross peaks that were approximately 10-15% of the diagonal peak intensity.

From LINEST

Slope	-6449.572174
Std Error slope	105.3916119
Intercept	22.55225921
Std Error Intercept	0.369614223
Student t-value, n-2, 0.05	3.18
Slope 95% Confidence interval	335.1453259
Intercept 95% Confidence interval	1.175373229

Using $$\ln\left(\frac{k}{T}\right) = -\frac{\Delta_r H^{\neq}}{R}\left(\frac{1}{T}\right) + \frac{\Delta_r S^{\neq}}{R} + \ln\left(\frac{k}{h}\right)$$

and $$\ln\left(\frac{k}{h}\right) = \ln(2.0836\text{x}10^{10}) = 23.7600$$

$\Delta H^{‡}$ = 53.6 ± 2.8 kJ mol^{-1}; $\Delta S^{‡}$ = –10.0 ± 9.8 J K^{-1} mol^{-1}
(95% confidence intervals)

Density Functional Theory Calculations

***Table 7S**:* Coordination number, point groups, energies and number of imaginary frequencies of calculated structures

Structure (description)	**CN**	**Point group**	**Type**	**Energy (no ZPE) Hartree**	**ZPE Hartree**	**Relative Energy (ZPE inc) kJ mol^{-1}**	**IF**
A. Calculated seven coordinate from X-ray	7	C_1	Minimum	-2846.57401	0.57929	0	0
B. Seven coordinate Cs symmetry	7	C_s	2nd order saddle point	-2846.55079	0.57751	56.3	2
C. Transition structure (close to Cs geometry)	7	C_1	Transition state	-2846.55219	0.57784	53.5	1
D. Optimized C_{2v} structure	6/7	C_{2v}	Higher order saddle point	-2846.47473	0.57786	256.9	6
E. One axial pyridyl uncoordinated	6	C_1	Minimum	-2846.57057	0.57882	7.8	0
F. One axial pyridyl uncoordinated	6	C_1	Minimum	-2846.57003	0.57879	9.1	0
G. One equatorial pyridyl uncoordinated	6	C_1	Minimum	-2846.55860	0.57815	37.5	0
H. One equatorial pyridyl uncoordinated	6	C_1	Minimum	-2846.55863	0.57826	37.7	0

CN – coordination number; IF – imaginary frequencies

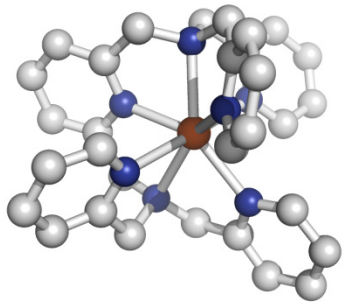
***Table 8S**:* Comparison of metric parameters of X-ray and DFT calculated structures

	Bond lengths (Å)				
	DFT	X-ray		DFT	X-ray
M–N1	2.272	2.219(3)	M–N5	2.473	2.539(3)
M–N2	2.364	2.331(3)	M–N6	2.350	2.261(3)
M–N3	2.428	2.347(3)	M–N7	2.410	2.326(3)
M–N4	2.245	2.167(3)			
	Bond angles (°)				
	DFT	X-ray		DFT	X-ray
N1–M–N2	105.4	109.5(1)	N3–M–N4	69.5	71.0(1)
N1–M–N3	72.2	72.5(1)	N3–M–N5	109.8	108.6(1)
N1–M–N4	123.3	122.4(1)	N3–M–N6	143.1	139.9(1)
N1–M–N5	80.3	77.5(1)	N3–M–N7	139.9	143.5(1)
N1–M–N6	89.6	87.0(1)	N4–M–N5	75.2	74.0(1)
N1–M–N7	143.1	138.7(1)	N4–M–N6	143.5	146.1(1)
N2–M–N3	70.8	72.6(1)	N4–M–N7	72.5	74.3(1)
N2–M–N4	99.7	100.0(1)	N5–M–N6	97.9	99.7(1)
N2–M–N5	173.9	172.8(1)	N5–M–N7	71.8	71.6(1)
N2–M–N6	84.2	82.9(1)	N6–M–N7	71.3	72.2(1)
N2–M–N7	103.7	103.1(1)			

Table 8S compares important metric parameters found in the X-ray structure and lowest energy DFT structure. The latter was calculated by performing a geometry optimization of the X-ray structure which had been modified to make the initial C-H bond lengths 1.085 Å and 1.100 Å for sp^2 and sp^3 carbons respectively. The distorted pentagonal bipyramidal geometry is retained in both structures. There are minor differences between the Fe-N distances between DFT calculated and X-ray structures, which are 0.05 Å longer on average in the DFT case (maximum difference 0.09 Å; RMSD 0.07 Å). The N-Fe-N angles differ by up to 4.4º with an RMSD of 2.2º.

Coordinates of calculated structures

A. Calculated seven coordinate minimum (starting from X-ray structure) (E_{rel} = 0 kJ mol^{-1})



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C	-4.419823001	-1.350926000	-1.466973000
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C	1.007310000	0.256571000	-2.984108000
C	-3.277574000	-0.631684000	-1.131378000
C	-3.218823000	4.087553000	-0.628148000
C	-1.617600000	2.461304000	-1.397233000
N	0.416902000	1.199084000	-2.004606000
C	-3.250351000	-3.334492000	-0.811788000
N	-2.144529000	-1.199428000	-0.668911000
C	1.819049000	-0.828936000	-2.309164000
C	2.934334000	-1.419818000	-2.901400000
C	1.370699000	2.280137000	-1.643762000
C	-2.140317000	-2.542026000	-0.514287000
C	-3.193501000	3.459655000	0.615971000
N	-1.565741000	1.868436000	-0.183234000
N	1.348876000	-1.240601000	-1.120660000
C	3.563136000	-2.474615000	-2.238566000
C	-2.353721000	2.362550000	0.790680000
FE	-0.193010000	-0.031745000	-0.02448100
C	-0.852284000	-3.178434000	-0.047257000
C	2.393829000	1.880052000	-0.607461000
C	3.707204000	2.348517000	-0.676270000
C	1.949212000	-2.257437000	-0.476793000
C	3.060363000	-2.908042000	-1.010911000
N	1.946482000	1.127776000	0.415516000
N	-0.099827000	-2.290938000	0.859572000
C	4.593718001	2.039709000	0.354865000
C	1.334372000	-2.632000000	0.857084000
N	-0.290323000	0.105306000	2.240938000
C	-0.687927000	-2.301359000	2.210190000
C	2.811299000	0.831668000	1.400881000
C	-0.075439000	1.264968000	2.896364000
C	4.134988000	1.264727000	1.419045000
C	-0.396832000	-1.026413000	2.968847000
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C	-0.296675000	-1.025169000	4.361623001
C	-0.096814000	0.180537000	5.031000001
H	-2.416684000	4.031295000	-2.635300000
H	-5.297272001	-0.831580000	-1.837199000
H	-1.440705000	0.999053000	-2.943754000
H	-0.639877000	2.525229000	-3.318286000
H	0.184545000	-0.226886000	-3.524366000
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H	1.867968000	2.666043000	-2.544643000
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H	-3.806076000	3.809752000	1.439975000
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H	4.430570001	-2.958381000	-2.677054000
H	-1.057262000	-4.151183000	0.423146000
H	-2.314617000	1.848848000	1.744501000
H	3.520756000	-3.735100000	-0.479547000
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H	5.618815001	2.396234000	0.326421000
H	1.505049000	-3.697945000	1.072826000
H	0.038966000	2.146221000	2.275042000
H	1.820165000	-2.063442000	1.658950000
H	-0.361262000	-3.176161000	2.791443000
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H	-0.377541000	-1.958899000	4.909588001
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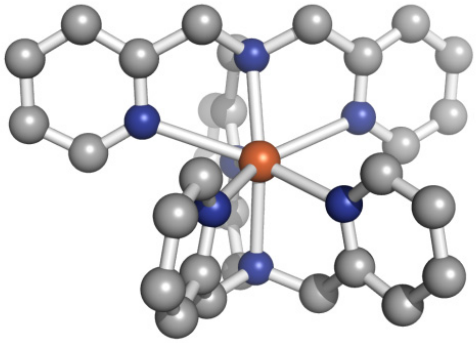
B. Seven coordinate, Cs symmetry
(E_{rel} = 56.3 kJ mol^{-1})



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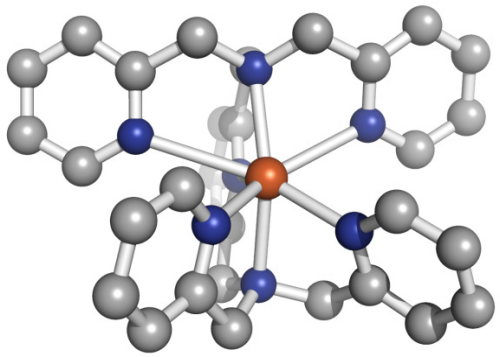
C	-1.378112000	2.609220000	0.000000000
C	-2.804457000	0.767121000	0.000000000
C	-2.455865000	3.493942000	0.000000000
C	-3.928374000	1.592120000	0.000000000
C	-3.749324000	2.974649000	0.000000000
C	2.312239000	-1.488238000	1.840007000
C	2.312239000	-1.488238000	-1.840007000
C	-0.821094000	0.310036000	3.525426000
C	-0.821094000	0.310036000	-3.525426000
C	0.050629000	3.133054000	0.000000000
C	-2.973287000	-0.743848000	0.000000000
C	3.503105000	-1.604446000	2.549300000
C	3.503105000	-1.604446000	-2.549300000
C	-1.360506000	-0.074282000	4.751140001
C	-1.360506000	-0.074282000	-4.751140001
C	4.244268001	-0.447728000	2.792524000
C	4.244268001	-0.447728000	-2.792524000
C	-2.042675000	-1.288993000	4.822744001
C	-2.042675000	-1.288993000	-4.822744001
C	3.758041000	0.772967000	2.325784000
C	3.758041000	0.772967000	-2.325784000
C	-2.160209000	-2.061939000	3.667631000
C	-2.160209000	-2.061939000	-3.667631000
C	1.918146000	2.123940000	1.229986000
C	1.918146000	2.123940000	-1.229986000
C	-1.637136000	-2.408218000	1.208669000
C	-1.637136000	-2.408218000	-1.208669000
C	2.546039000	0.804563000	1.634006000
C	2.546039000	0.804563000	-1.634006000
C	-1.578826000	-1.598291000	2.485266000
C	-1.578826000	-1.598291000	-2.485266000
N	1.088858000	2.064171000	0.000000000
N	-1.704703000	-1.543364000	0.000000000
N	-1.561966000	1.279069000	0.000000000
N	1.837138000	-0.314157000	1.388740000
N	1.837138000	-0.314157000	-1.388740000
N	-0.917840000	-0.431369000	2.411380000
N	-0.917840000	-0.431369000	-2.411380000
FE	0.081408000	-0.068026000	0.00000000
H	-4.607805001	3.639216000	0.000000000
H	0.185343000	3.785474000	0.869824000
H	0.185343000	3.785474000	-0.869824000
H	-3.571979000	-1.020388000	0.874787000
H	-3.571979000	-1.020388000	-0.874787000
H	2.694390000	2.898019000	1.143110000
H	2.694390000	2.898019000	-1.143110000
H	-0.735302000	-3.028333000	1.119275000
H	-0.735302000	-3.028333000	-1.119275000
H	-2.285739000	4.566449001	0.000000000
H	-4.924992001	1.161063000	0.000000000
H	4.307581001	1.692661000	2.501850000
H	4.307581001	1.692661000	-2.501850000
H	-2.693865000	-3.007631000	3.683084000
H	-2.693865000	-3.007631000	-3.683084000
H	5.183724001	-0.494375000	3.334661000
H	5.183724001	-0.494375000	-3.334661000
H	-2.482759000	-1.624677000	5.756734001
H	-2.482759000	-1.624677000	-5.756734001
H	3.839346000	-2.576135000	2.894683000
H	3.839346000	-2.576135000	-2.894683000
H	-1.252325000	0.564855000	5.621116001
H	-1.252325000	0.564855000	-5.621116001
H	1.710586000	-2.366874000	1.623767000
H	1.710586000	-2.366874000	-1.623767000
H	-0.288184000	1.252819000	3.431403000
H	-0.288184000	1.252819000	-3.431403000
H	1.260030000	2.431048000	2.050360000
H	1.260030000	2.431048000	-2.050360000
H	-2.490352000	-3.101374000	1.238598000
H	-2.490352000	-3.101374000	-1.238598000

C. Transition structure (distorted from Cs geometry)
(E_{rel} = 53.5 kJ mol^{-1})



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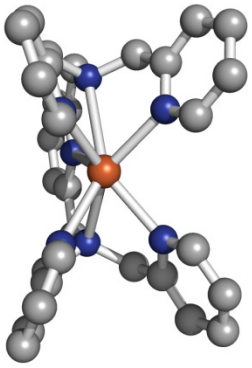
C	-0.233600000	0.329600000	-0.092300000
C	-0.129000000	0.029000000	2.217100000
C	1.153400000	0.357100000	-0.196500000
C	1.266900000	0.072000000	2.191900000
C	1.913800000	0.219400000	0.967500000
C	-5.393600001	-2.156100000	0.616100000
C	-5.333500001	2.009600000	1.195500000
C	-2.092900000	-3.603800000	1.618400000
C	-1.867300000	3.677700000	1.477000000
C	-1.142200000	0.643700000	-1.264400000
C	-0.874000000	-0.141500000	3.528200000
C	-6.085400001	-3.161500000	-0.052700000
C	-6.170400001	3.013600000	0.728500000
C	-2.043900000	-4.815200001	2.303400000
C	-1.370300000	4.792100001	2.153300000
C	-5.581900001	-3.616500000	-1.271600000
C	-6.091900001	3.366800000	-0.620300000
C	-2.346100000	-4.819900001	3.665500000
C	-1.305100000	4.745100001	3.545000000
C	-4.415100001	-3.041300000	-1.776500000
C	-5.197100001	2.685000000	-1.440300000
C	-2.669600000	-3.613100000	4.284300001
C	-1.740700000	3.591400000	4.199100001
C	-2.505700000	-1.373200000	-1.523100000
C	-3.535700000	0.826800000	-1.817400000
C	-3.039900000	-1.109200000	4.132800000
C	-2.789400000	1.286400000	4.093300000
C	-3.779200000	-2.040000000	-1.042300000
C	-4.410300001	1.663700000	-0.899700000
C	-2.694200000	-2.446700000	3.516000000
C	-2.232500000	2.529600000	3.436000000
N	-2.486400000	0.048200000	-1.113900000
N	-2.361300000	0.017600000	3.435200000
N	-0.847800000	0.133200000	1.090500000
N	-4.261400001	-1.607900000	0.141900000
N	-4.466800001	1.341900000	0.407500000
N	-2.416600000	-2.437700000	2.201200000
N	-2.291600000	2.567300000	2.095000000
Fe	-2.965100000	-0.074900000	1.169900000
H	2.998100000	0.240900000	0.919300000
H	-0.671200000	0.349800000	-2.213500000
H	-1.267100000	1.732400000	-1.298800000
H	-0.645100000	-1.135600000	3.923600000
H	-0.471300000	0.574300000	4.254700001
H	-2.404500000	-1.483700000	-2.612900000
H	-4.193800001	0.127600000	-2.345900000
H	-4.122000000	-0.930800000	4.073600000
H	-3.885800000	1.314600000	4.057900000
H	1.629800000	0.499100000	-1.161400000
H	1.834000000	-0.011500000	3.114000000
H	-4.006200000	-3.359500000	-2.730700000
H	-5.114100001	2.930700000	-2.494900000
H	-2.893700000	-3.574500000	5.346200001
H	-1.705900000	3.521600000	5.282300001
H	-6.094400001	-4.396300001	-1.826500000
H	-6.716600001	4.157300000	-1.024600000
H	-2.318600000	-5.742100001	4.237800001
H	-0.922000000	5.587800001	4.112300000
H	-6.996800001	-3.569400000	0.371000000
H	-6.856100001	3.510700000	1.406000000
H	-1.770600000	-5.726700001	1.782200000
H	-1.044700000	5.668000001	1.601900000
H	-5.754900001	-1.772500000	1.566300000
H	-5.345300001	1.725500000	2.243100000
H	-1.866700000	-3.565400000	0.556700000
H	-1.937100000	3.679400000	0.391200000
H	-1.632400000	-1.858900000	-1.070400000
H	-3.094800000	1.463000000	-2.594200000
H	-2.784500000	-1.114900000	5.202700001
H	-2.510200000	1.269200000	5.156500001

D. Optimized C_{2v} structure
(E_{rel} = 256.9 kJ mol^{-1})



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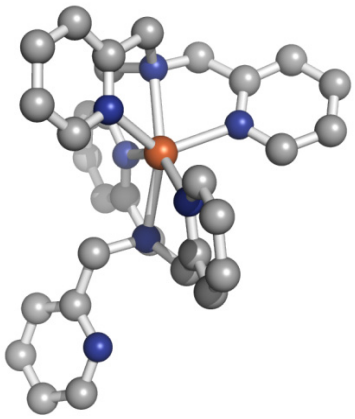
C	2.641109000	3.928046000	2.295904000
C	2.641109000	-3.928046000	2.295904000
C	2.387181000	2.763209000	3.014953000
C	2.387181000	-2.763209000	3.014953000
C	2.220755000	3.976875000	0.971581000
C	2.220755000	-3.976875000	0.971581000
C	1.752796000	1.712425000	2.365459000
C	1.752796000	-1.712425000	2.365459000
C	1.599994000	2.867902000	0.385977000
C	1.599994000	-2.867902000	0.385977000
N	1.383074000	1.720071000	1.067338000
N	1.383074000	-1.720071000	1.067338000
C	1.247461000	2.956887000	-1.075429000
C	1.247461000	-2.956887000	-1.075429000
FE	0.000000000	0.000000000	0.185160000
N	0.000000000	2.308570000	-1.529318000
N	0.000000000	-2.308570000	-1.529318000
C	0.000000000	-2.432060000	-3.019702000
C	0.000000000	2.432060000	-3.019702000
N	0.000000000	0.000000000	-3.097599000
C	0.000000000	1.140437000	-3.791331000
C	0.000000000	-1.140437000	-3.791331000
C	0.000000000	1.194817000	-5.187732001
C	0.000000000	-1.194817000	-5.187732001
C	0.000000000	0.000000000	-5.900934001
C	-1.247461000	2.956887000	-1.075429000
C	-1.247461000	-2.956887000	-1.075429000
N	-1.383074000	1.720071000	1.067338000
N	-1.383074000	-1.720071000	1.067338000
C	-1.599994000	2.867902000	0.385977000
C	-1.599994000	-2.867902000	0.385977000
C	-1.752796000	1.712425000	2.365459000
C	-1.752796000	-1.712425000	2.365459000
C	-2.220755000	-3.976875000	0.971581000
C	-2.220755000	3.976875000	0.971581000
C	-2.387181000	2.763209000	3.014953000
C	-2.387181000	-2.763209000	3.014953000
C	-2.641109000	3.928046000	2.295904000
C	-2.641109000	-3.928046000	2.295904000
H	3.133818000	4.778975001	2.755889000
H	3.133818000	-4.778975001	2.755889000
H	2.661397000	2.664330000	4.059718000
H	2.661397000	-2.664330000	4.059718000
H	2.373523000	4.872626001	0.378348000
H	2.373523000	-4.872626001	0.378348000
H	2.059726000	2.475726000	-1.634563000
H	2.059726000	-2.475726000	-1.634563000
H	1.512398000	0.827280000	2.930909000
H	1.512398000	-0.827280000	2.930909000
H	1.259198000	4.020348000	-1.362003000
H	1.259198000	-4.020348000	-1.362003000
H	0.866862000	3.023681000	-3.335392000
H	0.866862000	-3.023681000	-3.335392000
H	0.000000000	2.152054000	-5.701464001
H	0.000000000	-2.152054000	-5.701464001
H	0.000000000	0.000000000	-6.986574001
H	-0.866862000	-3.023681000	-3.335392000
H	-0.866862000	3.023681000	-3.335392000
H	-1.259198000	4.020348000	-1.362003000
H	-1.259198000	-4.020348000	-1.362003000
H	-1.512398000	0.827280000	2.930909000
H	-1.512398000	-0.827280000	2.930909000
H	-2.059726000	2.475726000	-1.634563000
H	-2.059726000	-2.475726000	-1.634563000
H	-2.373523000	4.872626001	0.378348000
H	-2.373523000	-4.872626001	0.378348000
H	-2.661397000	2.664330000	4.059718000
H	-2.661397000	-2.664330000	4.059718000
H	-3.133818000	4.778975001	2.755889000
H	-3.133818000	-4.778975001	2.755889000

E. Axial pyridyl uncoordinated, isomer 1 (E_{rel} = 7.8 kJ mol^{-1})



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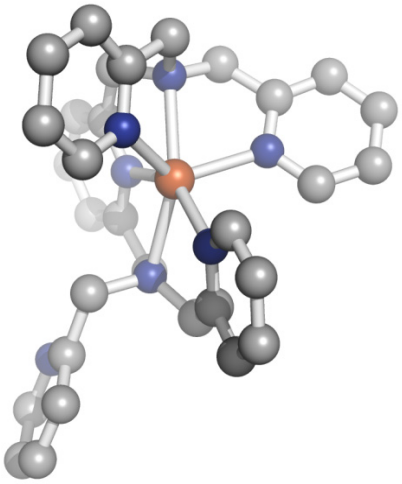
C	0.733015000	-4.707742001	-0.683728000
C	1.491847000	-3.661628000	-1.209254000
C	-4.240226001	0.927566000	-3.488796000
C	-0.437772000	-4.417891001	0.019355000
C	-4.327361001	-0.156203000	-2.616716000
C	1.050857000	-2.353373000	-1.017624000
C	1.747460000	-1.148230000	-1.609616000
C	-3.125637000	1.762872000	-3.410559000
C	-3.298336000	-0.384165000	-1.703185000
C	-3.310887000	-1.607581000	-0.812728000
C	-0.806157000	-3.084744000	0.186361000
N	-0.070296000	-2.079268000	-0.325760000
C	-2.153260000	1.484448000	-2.457599000
N	-2.222616000	0.431058000	-1.615530000
C	1.716865000	1.307719000	-1.504679000
N	1.533528000	0.039963000	-0.752756000
C	5.977850001	-1.341814000	0.429541000
C	6.615107001	-0.234920000	-0.124660000
C	-2.026128000	-2.658813000	0.973583000
C	4.593402001	-1.296421000	0.614880000
C	5.838136001	0.873777000	-0.472833000
N	-2.567025000	-1.390999000	0.441007000
C	3.901056000	-0.139555000	0.245413000
FE	-0.705137000	0.010427000	-0.05494000
N	4.513851001	0.932459000	-0.290284000
C	2.404801000	-0.011200000	0.476957000
C	1.065760000	2.460265000	-0.774757000
N	-0.077378000	2.180264000	-0.111561000
C	1.590624000	3.751612000	-0.830653000
C	-3.361273000	-0.664576000	1.448132000
N	-1.239176000	0.347851000	2.082929000
C	-0.734523000	3.190981000	0.490447000
C	0.901673000	4.793244001	-0.210022000
C	-2.454829000	-0.068832000	2.505079000
C	-0.289685000	4.508550001	0.459083000
C	-0.406846000	0.908408000	2.983402000
C	-2.862233000	0.065553000	3.831520000
C	-0.738579000	1.073407000	4.323822001
C	-1.994460000	0.646901000	4.756185001
H	1.047058000	-5.737613001	-0.823303000
H	2.403476000	-3.855305000	-1.765436000
H	-5.028687001	1.118445000	-4.210315001
H	1.308752000	-0.940706000	-2.593472000
H	-5.181855001	-0.825276000	-2.645565000
H	2.812241000	-1.353115000	-1.771679000
H	-2.822351000	-2.427060000	-1.353316000
H	-1.051323000	-5.211818001	0.433287000
H	-3.013180000	2.620342000	-4.065153000
H	1.227583000	1.184191000	-2.479751000
H	-4.343981001	-1.931664000	-0.621643000
H	2.775744000	1.519275000	-1.677978000
H	-1.286226000	2.124835000	-2.347793000
H	6.544006001	-2.222529000	0.717710000
H	-2.784113000	-3.455154000	0.979446000
H	7.688522001	-0.221583000	-0.282523000
H	4.066809000	-2.139608000	1.053732000
H	6.300792001	1.756645000	-0.907942000
H	2.054828000	-0.850057000	1.086334000
H	2.526326000	3.930105000	-1.350304000
H	-1.733906000	-2.491830000	2.016719000
H	-3.898052000	0.141421000	0.931861000
H	-4.123649000	-1.306377000	1.913338000
H	2.212826000	0.912507000	1.029873000
H	-1.647208000	2.924800000	1.014902000
H	1.290123000	5.806515001	-0.243450000
H	0.554812000	1.238383000	2.605407000
H	-0.859862000	5.286404001	0.955625000
H	-3.844561000	-0.283820000	4.133994000
H	-0.027492000	1.525133000	5.007027001
H	-2.291676000	0.758429000	5.794402001

F. Axial pyridyl uncoordinated, isomer 2 (E_{rel} = 9.1 kJ mol^{-1})



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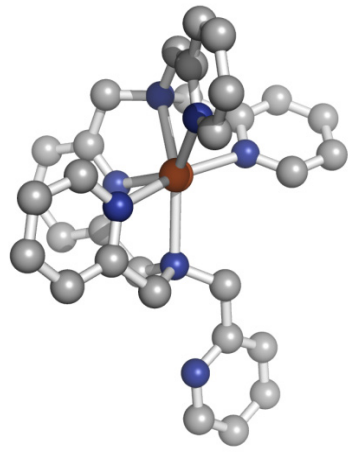
C	0.975000000	0.086000000	0.457000000
C	0.946000000	0.042000000	1.851000000
C	6.828000001	-4.753000001	3.106000000
C	2.205000000	0.074000000	-0.204000000
C	6.517000001	-4.094000000	1.919000000
C	2.154000000	-0.017000000	2.543000000
C	2.240000000	-0.151000000	4.044000000
C	6.666000001	-4.072000000	4.313000001
C	6.041000001	-2.784000000	1.966000000
C	5.599000001	-2.076000000	0.704000000
C	3.373000000	0.040000000	0.555000000
N	3.338000000	-0.003000000	1.901000000
C	6.210000001	-2.760000000	4.278000001
N	5.894000001	-2.116000000	3.134000000
C	3.866000000	0.052000000	5.876000001
N	3.459000000	0.540000000	4.542000001
C	0.002000000	2.935000000	5.901000001
C	0.271000000	3.680000000	7.053000001
C	4.756000001	0.084000000	-0.057000000
C	1.600000000	3.879000000	7.417000001
N	5.727000001	-0.612000000	0.814000000
C	2.240000000	2.609000000	5.474000001
Fe	5.198000001	-0.012000000	3.05300000
C	3.288000000	2.038000000	4.534000001
C	5.321000001	0.369000000	6.153000001
N	6.148000001	0.358000000	5.085000001
C	5.789000001	0.594000000	7.448000001
C	7.106000001	-0.149000000	0.582000000
N	6.597000001	1.539000000	2.262000000
C	7.464000001	0.558000000	5.291000001
C	7.154000001	0.794000000	7.654000001
C	7.293000001	1.247000000	1.139000000
C	8.011000001	0.772000000	6.552000001
C	6.748000001	2.764000000	2.805000000
C	8.151000001	2.168000000	0.540000000
C	7.581000001	3.738000000	2.265000000
C	8.301000001	3.432000000	1.110000000
C	2.605000000	3.332000000	6.614000001
N	0.956000000	2.414000000	5.121000001
H	0.050000000	0.127000000	-0.110000000
H	0.008000000	0.054000000	2.395000000
H	7.195000001	-5.775000001	3.090000000
H	2.332000000	-1.214000000	4.297000001
H	6.634000001	-4.591000001	0.960000000
H	1.333000000	0.238000000	4.515000001
H	4.540000001	-2.306000000	0.538000000
H	2.257000000	0.099000000	-1.288000000
H	6.898000001	-4.540000001	5.264000001
H	3.736000000	-1.038000000	5.887000001
H	6.145000001	-2.468000000	-0.166000000
H	3.228000000	0.454000000	6.672000001
H	6.095000001	-2.190000000	5.192000001
H	-1.024000000	2.759000000	5.585000001
H	4.746000001	-0.337000000	-1.073000000
H	-0.543000000	4.091000000	7.641000001
H	1.854000000	4.455000001	8.302000001
H	3.038000000	2.322000000	3.508000000
H	5.092000001	0.605000000	8.280000001
H	5.071000001	1.129000000	-0.150000000
H	7.783000001	-0.842000000	1.098000000
H	7.377000001	-0.176000000	-0.484000000
H	4.263000001	2.468000000	4.777000001
H	8.094000001	0.545000000	4.407000001
H	7.540000001	0.967000000	8.654000001
H	6.181000001	2.960000000	3.709000000
H	9.079000001	0.922000000	6.663000001
H	8.690000001	1.897000000	-0.362000000
H	7.658000001	4.710000001	2.740000000
H	8.962000001	4.165000000	0.657000000
H	3.652000000	3.480000000	6.863000001

G. Equatorial pyridyl uncoordinated, isomer 1
(E_{rel} = 37.5 kJ mol^{-1})



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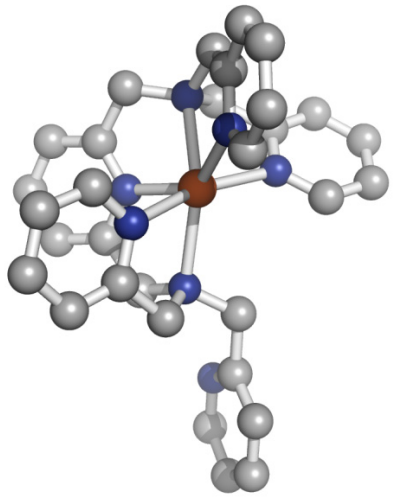
C	0.494700000	-0.848300000	0.114700000
C	-0.071700000	-1.110100000	2.560600000
C	1.227500000	-0.800100000	4.634500001
C	1.103000000	-1.314200000	-1.048100000
C	0.678300000	-1.544700000	1.312400000
N	0.421200000	-1.727300000	3.814600000
C	2.572800000	-0.975300000	6.800400001
C	-0.688100000	-2.324100000	4.596200001
C	2.065300000	-1.561100000	5.644600001
C	1.893600000	-2.464000000	-0.982400000
C	3.391900000	-1.742900000	7.632000001
N	1.457100000	-2.642900000	1.377900000
C	4.452000001	-1.883000000	2.511300000
C	5.801800001	-1.548300000	2.513000000
C	-2.532100000	-3.943500000	3.933900000
C	-1.182500000	-3.592100000	3.933700000
C	2.051700000	-3.085000000	0.248900000
N	2.322200000	-2.847300000	5.335400001
Fe	1.838300000	-3.537200000	3.35290000
N	3.994300000	-3.090500000	2.893000000
C	-2.929200000	-5.125200001	3.307800000
N	-0.240000000	-4.365900001	3.348900000
C	3.659700000	-3.069800000	7.298200001
C	6.722400001	-2.507900000	2.936600000
C	3.092500000	-3.600400000	6.138200001
C	-0.636200000	-5.494700001	2.728300000
C	-1.962100000	-5.913200001	2.683600000
C	4.884300001	-4.022600000	3.292600000
C	6.254800001	-3.760300000	3.333000000
C	3.228300000	-5.065300001	5.781200001
N	3.040500000	-5.373000001	4.333400001
C	4.343100001	-5.397600001	3.604800000
C	2.315000000	-6.672300001	4.179200000
C	2.857500000	-7.879700001	4.939200001
C	1.972300000	-8.863400001	5.391300001
N	4.185300000	-7.968200001	5.109300001
C	2.490500000	-9.995300001	6.022200001
C	4.671700001	-9.052900001	5.728300001
C	3.870000000	-10.095900001	6.193700001
H	-0.125200000	0.043200000	0.096900000
H	-0.065000000	-0.015300000	2.635500000
H	0.602600000	-0.050000000	5.142000001
H	2.341400000	0.057200000	7.042300001
H	1.894900000	-0.252000000	3.958300000
H	0.965000000	-0.789400000	-1.988400000
H	-1.122500000	-1.391000000	2.423900000
H	-1.515200000	-1.613100000	4.730000001
H	3.702400000	-1.168300000	2.185300000
H	6.119100001	-0.562000000	2.191900000
H	-3.260700000	-3.296700000	4.412800001
H	-0.308600000	-2.562400000	5.595500001
H	3.812700000	-1.310100000	8.534500001
H	2.385500000	-2.865100000	-1.861800000
H	-3.975000000	-5.416300001	3.295600000
H	7.784900001	-2.285400000	2.957300000
H	2.684100000	-3.961600000	0.352700000
H	4.286400001	-3.688600000	7.932600001
H	0.143100000	-6.078100001	2.248200000
H	-2.225300000	-6.829800001	2.166900000
H	2.453200000	-5.605300001	6.338600001
H	6.942400001	-4.532900001	3.662200000
H	4.184100000	-5.460900001	6.139700001
H	1.278700000	-6.503100001	4.486000001
H	4.168200000	-5.915700001	2.653000000
H	5.074300001	-6.000700001	4.148200000
H	2.298000000	-6.896500001	3.104900000
H	0.900500000	-8.752500001	5.250700001
H	1.828100000	-10.778900001	6.377800001
H	5.751500001	-9.087600001	5.853200001
H	4.317700001	-10.956000001	6.680600001

H. Equatorial pyridyl uncoordinated, isomer 2
(E_{rel} = 37.7 kJ mol^{-1})



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C	0.672600000	-1.013300000	-0.024200000
C	-0.072600000	-1.149300000	2.383400000
C	1.152200000	-0.780400000	4.490800001
C	1.332000000	-1.557000000	-1.123500000
C	0.743300000	-1.664000000	1.210400000
N	0.327600000	-1.710800000	3.694000000
C	2.328500000	-0.906300000	6.754600001
C	-0.848000000	-2.191400000	4.457800001
C	1.882900000	-1.523800000	5.592000001
C	2.059500000	-2.737900000	-0.957600000
C	3.043800000	-1.669200000	7.682600001
N	1.463900000	-2.791900000	1.374400000
C	4.478900001	-2.253600000	2.626000000
C	5.853200001	-2.044500000	2.686500000
C	-2.747500000	-3.760800000	3.840100000
C	-1.383500000	-3.472100000	3.854800000
C	2.107700000	-3.309800000	0.306200000
N	2.103500000	-2.834800000	5.358300001
Fe	1.658900000	-3.615900000	3.40730000
N	3.892300000	-3.396300000	3.027300000
C	-3.185100000	-4.958500001	3.274800000
N	-0.464100000	-4.320800001	3.341000000
C	3.273400000	-3.018900000	7.429100001
C	6.658400001	-3.065800000	3.191100000
C	2.775500000	-3.580400000	6.249600001
C	-0.899500000	-5.464500001	2.776300000
C	-2.241700000	-5.824500001	2.722000000
C	4.672300001	-4.387400001	3.507000000
C	6.057000001	-4.253700001	3.608000000
C	2.900200000	-5.062700001	5.975700001
N	2.677400000	-5.462700001	4.552400001
C	3.968200000	-5.679700001	3.851500000
C	1.835700000	-6.709400001	4.479200001
C	2.362100000	-7.932400001	5.211700001
C	2.561500000	-9.009100001	7.235700001
C	3.415600000	-10.094200001	5.276100001
C	3.197300000	-10.108600001	6.651400001
C	2.990900000	-8.984700001	4.540200001
N	2.146500000	-7.944800001	6.539800001
H	0.098300000	-0.096600000	-0.119800000
H	-0.048800000	-0.052200000	2.402500000
H	0.554300000	0.041100000	4.913100001
H	2.127200000	0.145500000	6.931900001
H	1.886400000	-0.324400000	3.815200000
H	1.281000000	-1.068600000	-2.091800000
H	-1.117800000	-1.421200000	2.195500000
H	-1.638100000	-1.428900000	4.504400001
H	3.816300000	-1.487100000	2.235600000
H	6.276700001	-1.105100000	2.347600000
H	-3.455600000	-3.054200000	4.261800001
H	-0.529200000	-2.381400000	5.488200001
H	3.412100000	-1.213300000	8.596500001
H	2.586700000	-3.200200000	-1.785000000
H	-4.242700001	-5.203000001	3.254000000
H	7.734800001	-2.941100000	3.258900000
H	2.689300000	-4.208500001	0.487900000
H	3.817600000	-3.634500000	8.138400001
H	-0.139000000	-6.110700001	2.350600000
H	-2.534900000	-6.758300001	2.254500000
H	2.170400000	-5.595900001	6.595100001
H	6.653700001	-5.071100001	4.000500000
H	3.876700000	-5.418000001	6.326600001
H	0.857900000	-6.451500001	4.892500001
H	3.748000000	-6.208900001	2.915100000
H	4.632300001	-6.333300001	4.430800001
H	1.711300000	-6.939500001	3.416700000
H	2.366800000	-8.987100001	8.305600001
H	3.898200000	-10.931600001	4.781300001
H	3.501900000	-10.952300001	7.262100001
H	3.131100000	-8.951800001	3.463000000