

Electronic supporting information

Spin transitions in ferric catecholate complexes mediated by outer-sphere counteranion

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Table S1. Crystallographic data for **1**, **3** and **4**.

Parameter	1		3		4	
Temperature/K	100.01(15)	293(2)	100.01(11)	293(2)	100.02(11)	293(2)
CCDC Number	2164135	2164133	2164128	2164127	2164130	2164132
Empirical formula	C ₃₂ H ₃₈ F ₆ FeN ₄ O ₂ P	C ₃₂ H ₃₈ F ₆ FeN ₄ O ₂ P	C ₃₂ H ₃₉ ClFeN ₄ O _{6.5}	C ₃₂ H ₃₉ ClFeN ₄ O _{6.5}	C ₃₂ H ₃₉ BF ₄ FeN ₄ O _{2.5}	C ₃₂ H _{38.66} BF ₄ FeN ₄ O _{2.33}
Formula weight	711.60	711.48	674.97	674.97	662.33	659.27
Crystal system	orthorhombic	orthorhombic	triclinic	triclinic	triclinic	triclinic
Space group	Pbcn	Pbcn	P-1	P-1	P-1	P-1
a/Å	23.8272(3)	24.0039(3)	8.3709(2)	8.5899(3)	8.3740(3)	8.5955(5)
b/Å	18.6423(2)	18.8295(2)	10.3122(2)	10.3201(3)	10.2623(3)	10.2994(4)
c/Å	15.0968(2)	15.30660(10)	19.7722(3)	20.3051(6)	19.6717(6)	20.1677(8)
α/°	90	90	97.511(2)	94.917(2)	97.060(2)	94.460(3)
β/°	90	90	92.574(2)	93.923(3)	93.064(3)	94.614(4)
γ/°	90	90	106.888(2)	106.867(3)	106.882(3)	106.445(4)
Volume/Å ³	6705.91(14)	6918.30(12)	1612.97(6)	1708.01(10)	1598.31(9)	1697.36(14)
Z	8	8	2	2	2	2
ρ _{calc} /cm ³	1.410	1.366	1.390	1.312	1.376	1.290
μ/mm ⁻¹	4.661	4.518	4.936	4.662	4.303	4.046
F(000)	2952.0	2952.0	708.0	708.0	692.0	689.0
Crystal size/mm ³	0.362 × 0.086 × 0.067	0.388 × 0.095 × 0.06	0.35 × 0.232 × 0.21	0.516 × 0.348 × 0.286	0.366 × 0.286 × 0.101	0.438 × 0.343 × 0.158
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.02 to 152.824	5.966 to 153	4.526 to 152.892	8.784 to 153.06	9.1 to 152.902	4.42 to 152.704
Index ranges	-28 ≤ h ≤ 29, -23 ≤ k ≤ 19, -18 ≤ l ≤ 18	-30 ≤ h ≤ 27, -23 ≤ k ≤ 23, -15 ≤ l ≤ 19	-10 ≤ h ≤ 10, -12 ≤ k ≤ 9, -24 ≤ l ≤ 24	-10 ≤ h ≤ 10, -13 ≤ k ≤ 12, -22 ≤ l ≤ 25	-10 ≤ h ≤ 10, -9 ≤ k ≤ 12, -24 ≤ l ≤ 24	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -24 ≤ l ≤ 25
Reflections collected	37644	104873	33846	35491	32634	27902
Independent reflections	7007 [R _{int} = 0.0274, R _{sigma} = 0.0198]	7262 [R _{int} = 0.1058, R _{sigma} = 0.0381]	6759 [R _{int} = 0.0289, R _{sigma} = 0.0214]	7137 [R _{int} = 0.0333, R _{sigma} = 0.0233]	6673 [R _{int} = 0.0550, R _{sigma} = 0.0408]	7070 [R _{int} = 0.0548, R _{sigma} = 0.0399]
Data/restraints/parameters	7007/0/451	7262/0/442	6759/10/452	7137/0/565	6673/0/455	7070/40/483
Goodness-of-fit on F ²	1.023	1.056	1.039	1.026	1.042	1.019
Final R indexes [I > 2σ (I)]	R ₁ = 0.0339, wR ₂ = 0.0842	R ₁ = 0.0467, wR ₂ = 0.1256	R ₁ = 0.0355, wR ₂ = 0.0925	R ₁ = 0.0418, wR ₂ = 0.1149	R ₁ = 0.0519, wR ₂ = 0.1264	R ₁ = 0.0589, wR ₂ = 0.1612
Final R indexes [all data]	R ₁ = 0.0380, wR ₂ = 0.0877	R ₁ = 0.0537, wR ₂ = 0.1332	R ₁ = 0.0369, wR ₂ = 0.0941	R ₁ = 0.0468, wR ₂ = 0.1220	R ₁ = 0.0576, wR ₂ = 0.1317	R ₁ = 0.0799, wR ₂ = 0.1818
Largest diff. peak/hole / e Å ⁻³	0.62/-0.65	0.52/-0.50	0.31/-0.66	0.22/-0.27	0.53/-0.45	0.32/-0.42

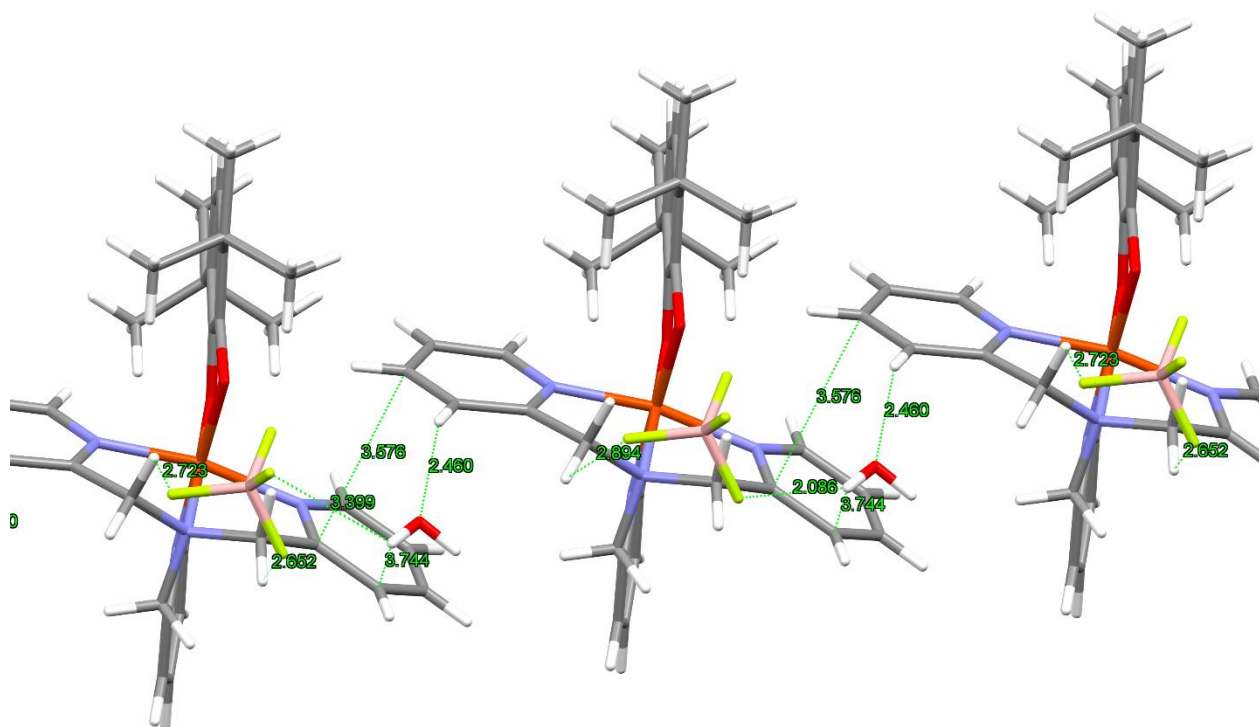


Fig. S1 Fragment of crystal packing and intermolecular interactions of complex **4**.

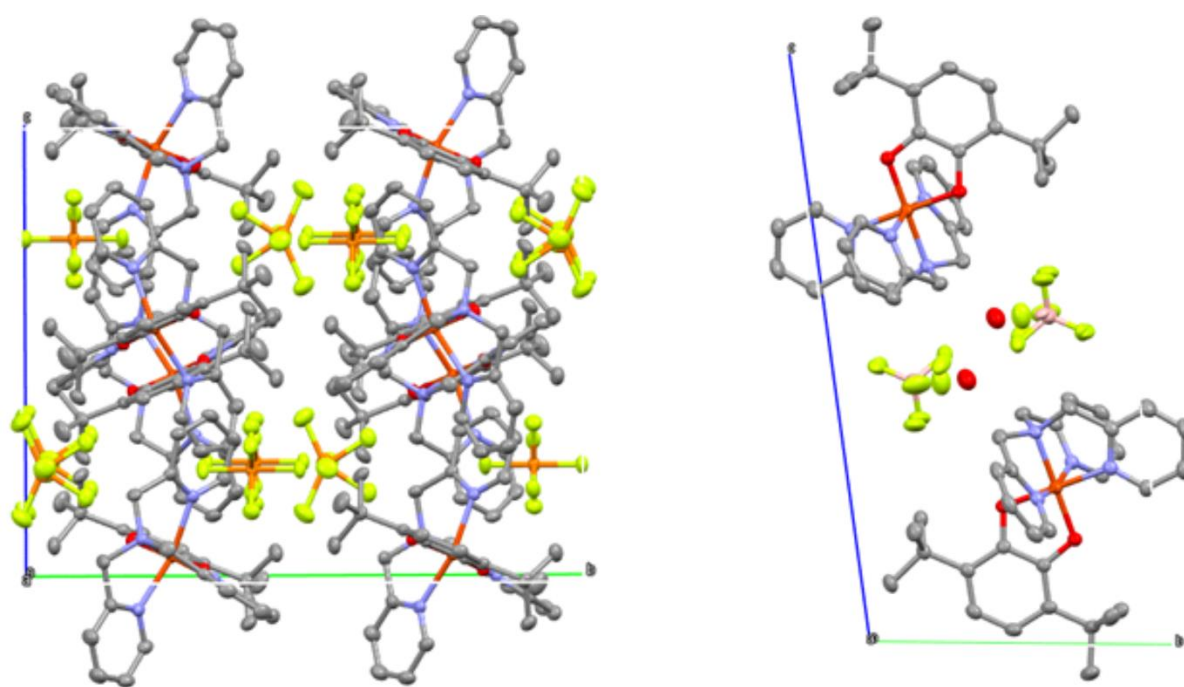


Fig. S2 Packing diagrams of **1** (left) and **4** (right) at 100 K in the *bc* plane (view along the *a* axis). Hydrogen atoms are omitted for clarity.

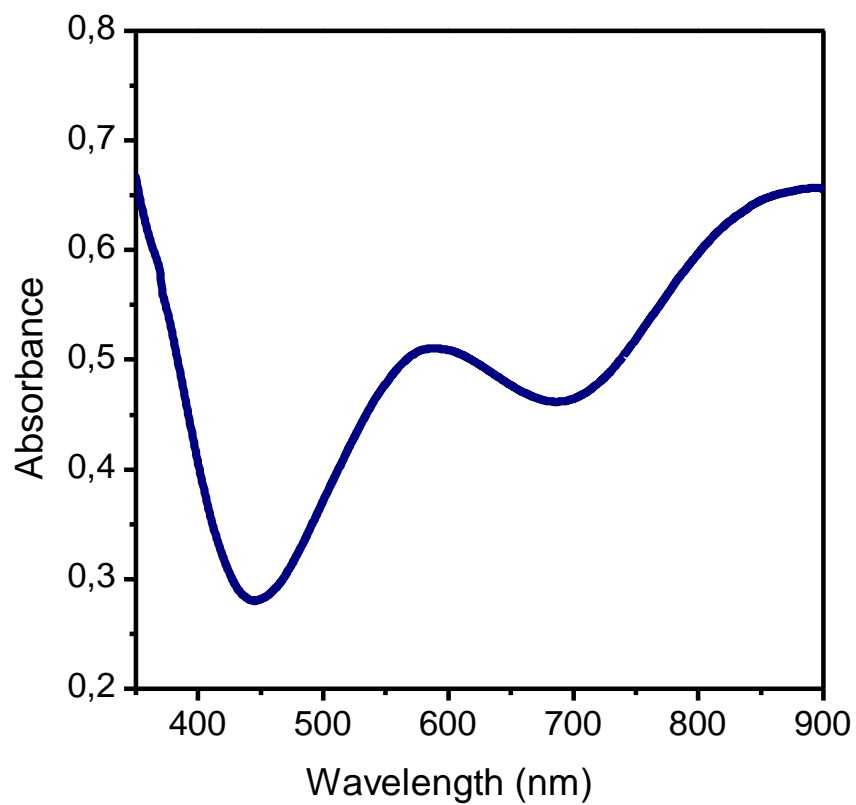


Fig. S3 UV-Vis spectrum of **4** in acetone at 298K ($C = 3 \cdot 10^{-4}$ M).

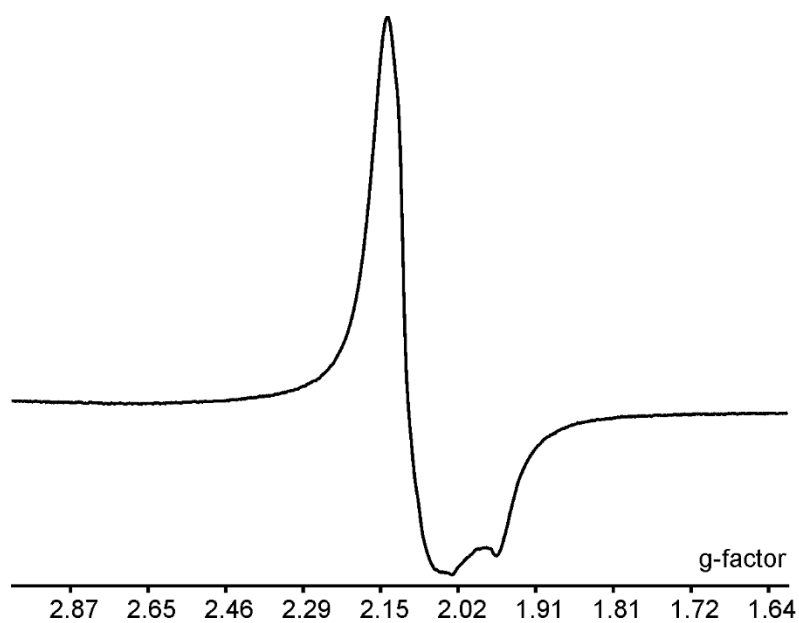


Fig. S4 X-Band EPR spectrum of low-spin isomer of **3** in frozen CH_2Cl_2 solution at 150 K.

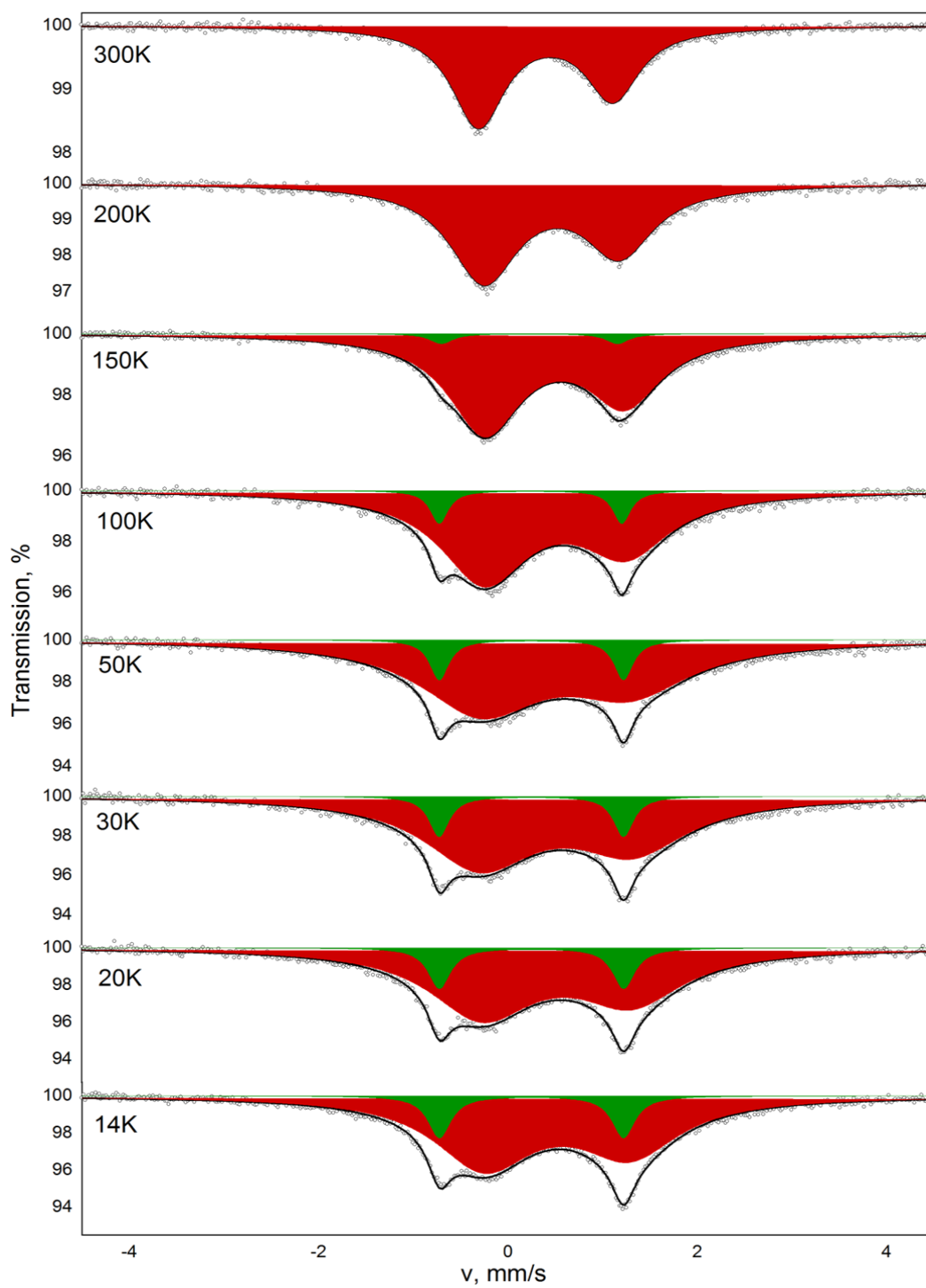


Fig. S5 Variable temperature ^{57}Fe Mössbauer spectra of **1** (hs- Fe^{III} – red, ls- Fe^{III} - green).

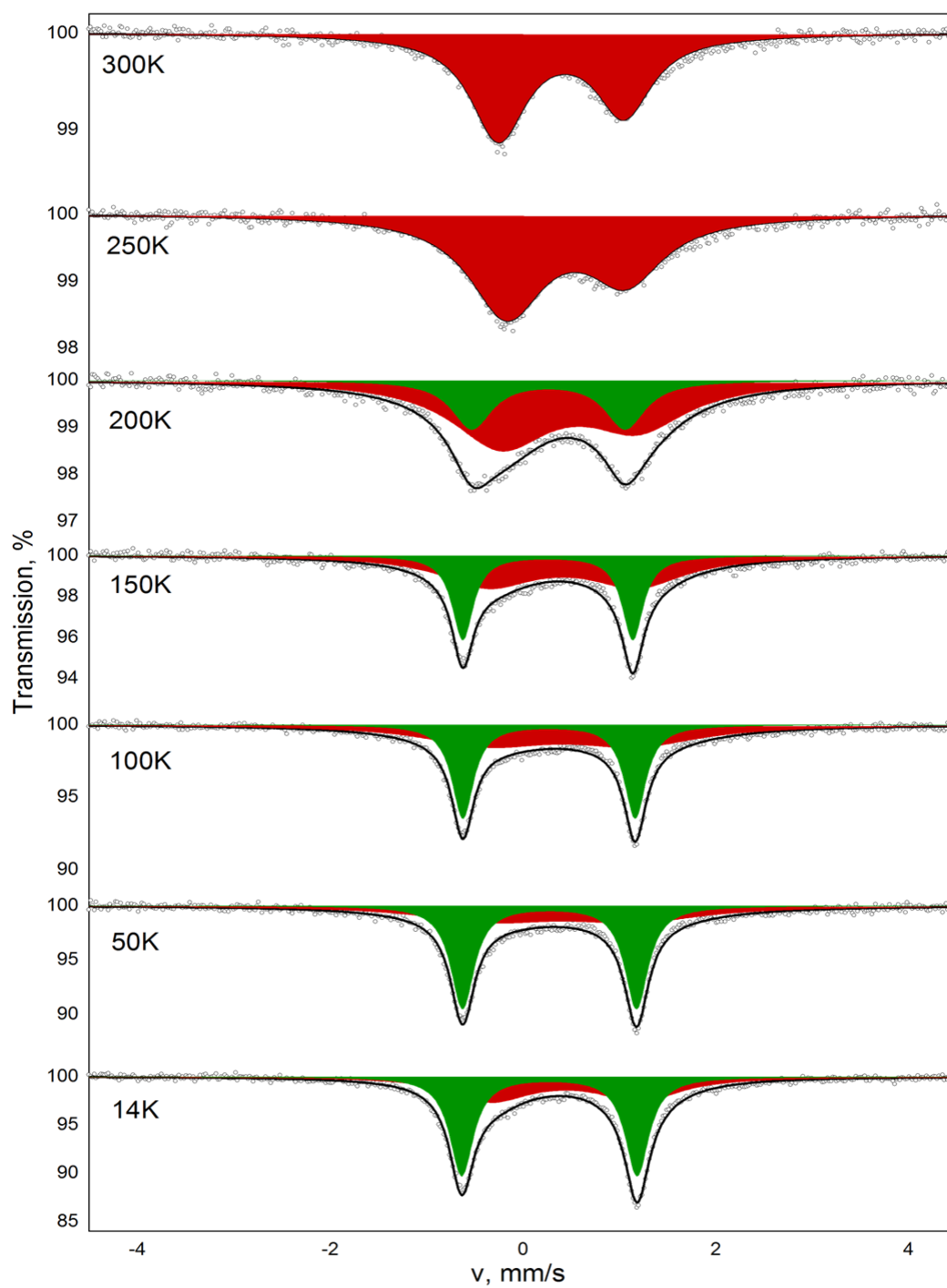


Fig. S6 Variable temperature ^{57}Fe Mössbauer spectra of **2** (hs- Fe^{III} – red, ls- Fe^{III} - green).

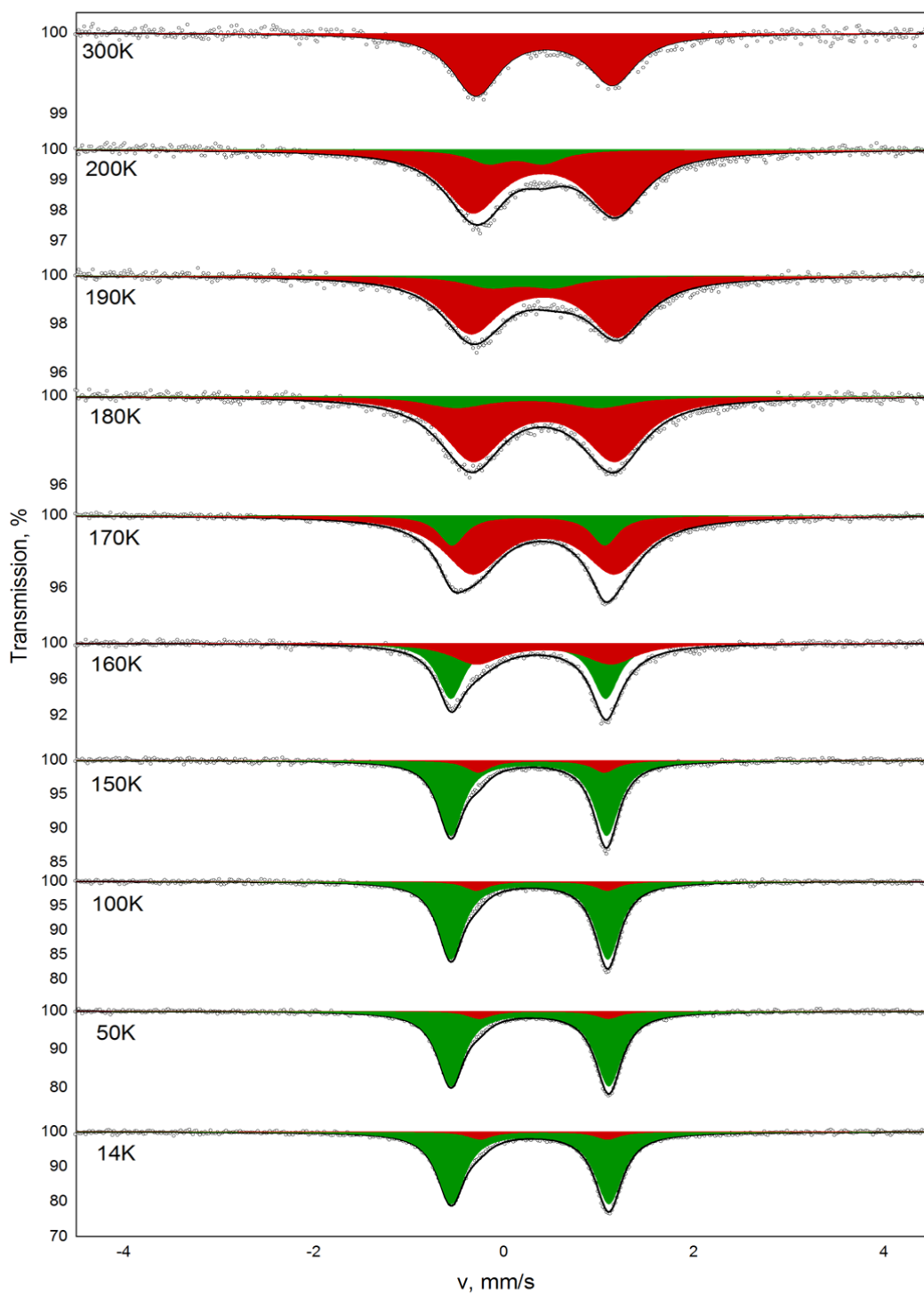


Fig. S7 Variable temperature ^{57}Fe Mössbauer spectra of **3** (hs-Fe^{III} – red, ls-Fe^{III} - green).

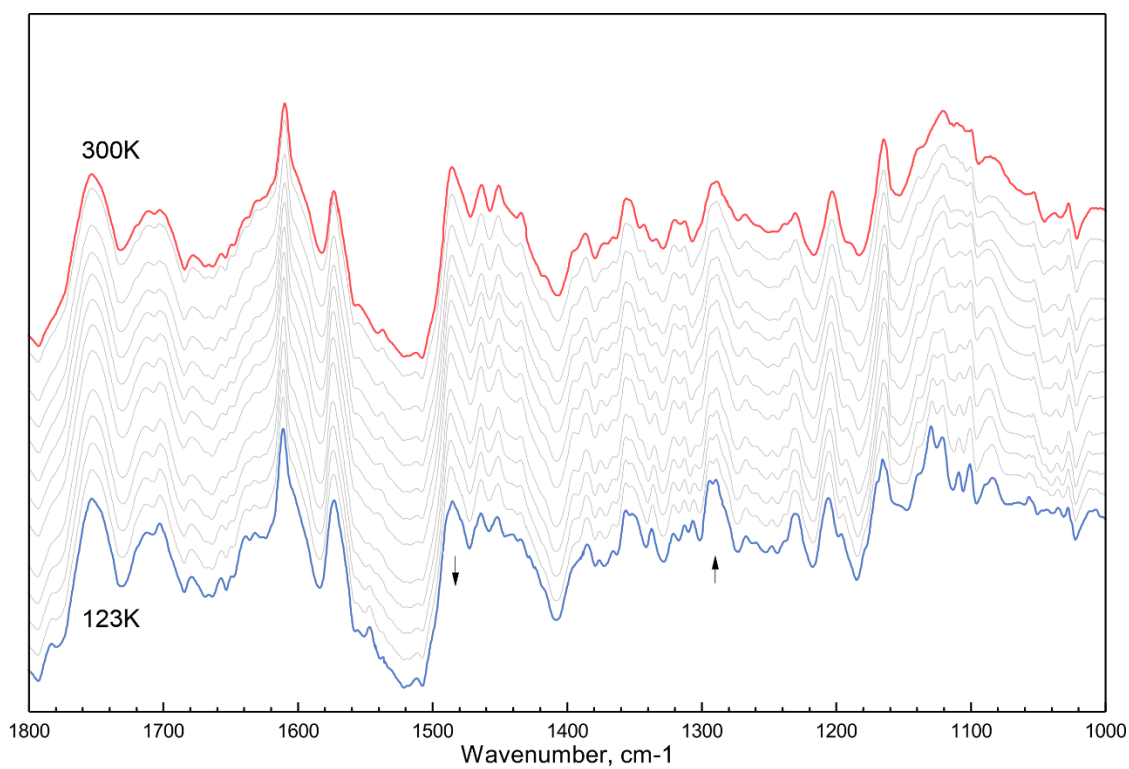


Fig. S8 DRIFT spectra of **4** measured in the interval from 300 K to 123 K.

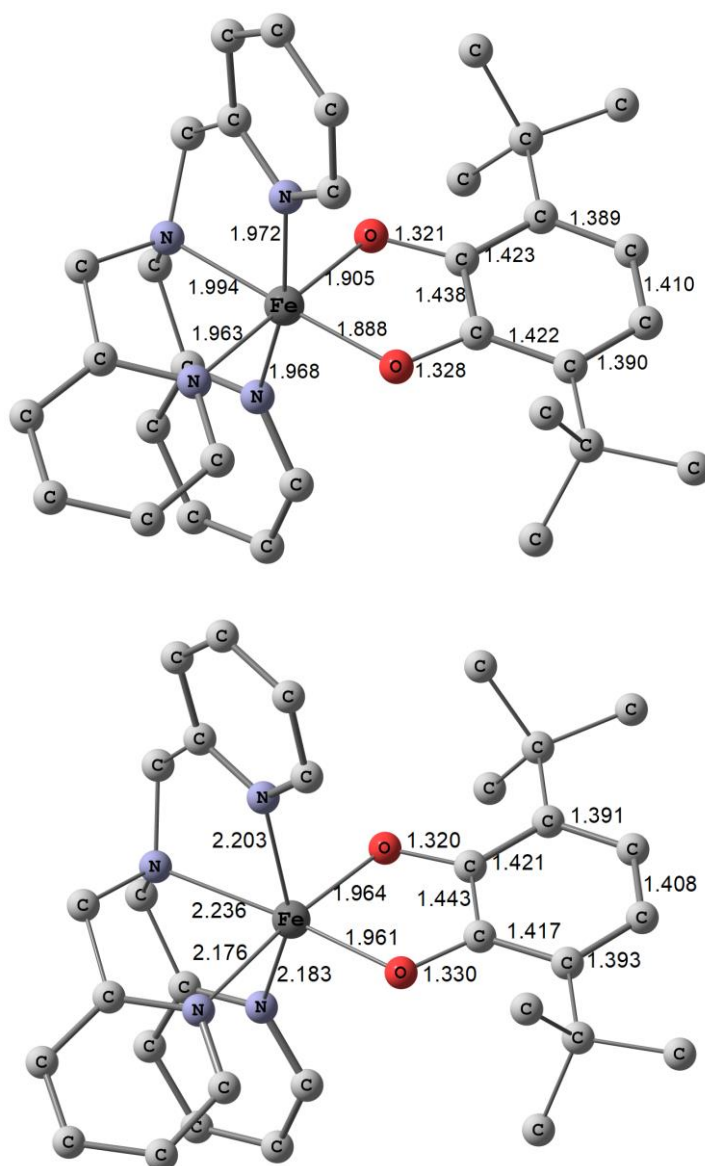


Fig. S9 Optimized geometries of cation **3⁺** in the low-spin (top) and high-spin (bottom) states according to the DFT calculations (UTPSSh/6-311++G(d,p)). Bond lengths are given in Å.

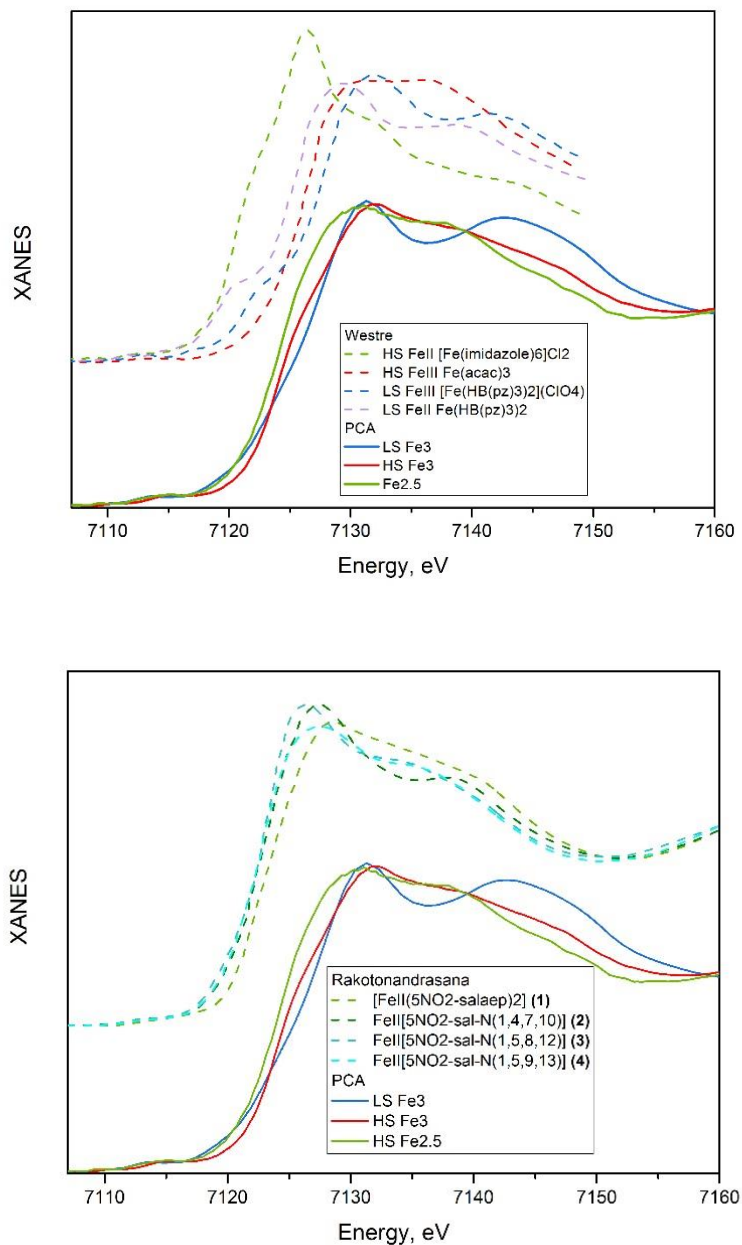
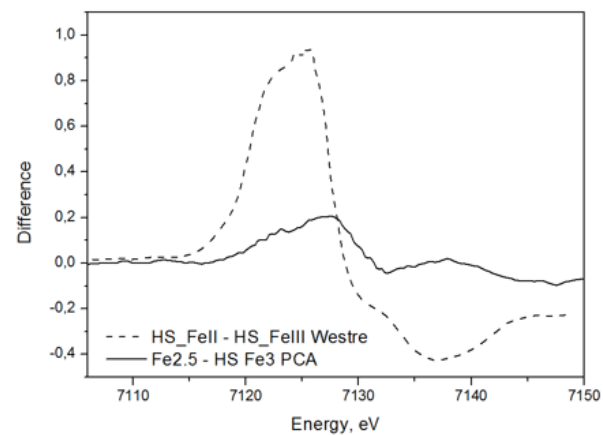
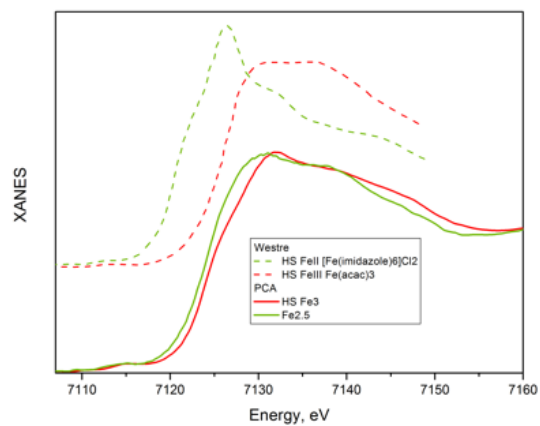
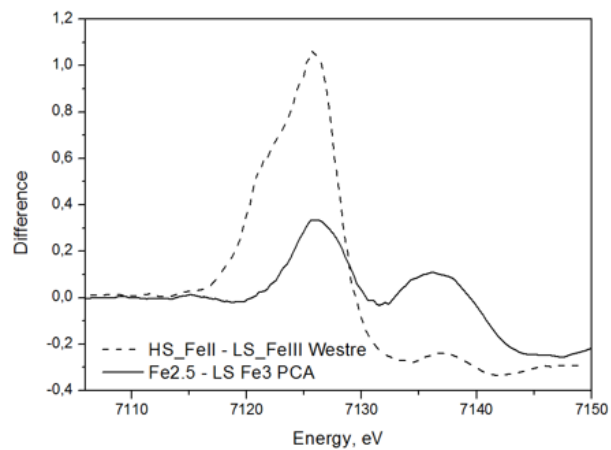
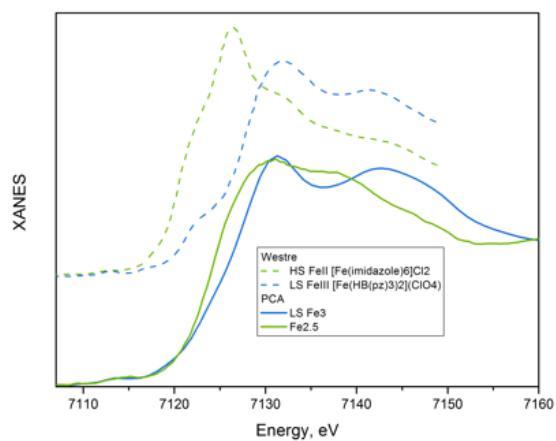
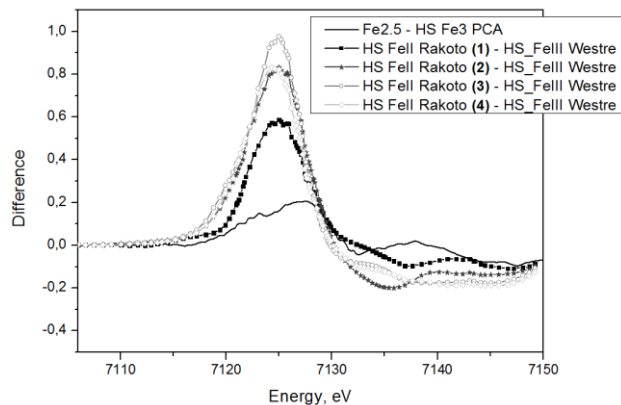
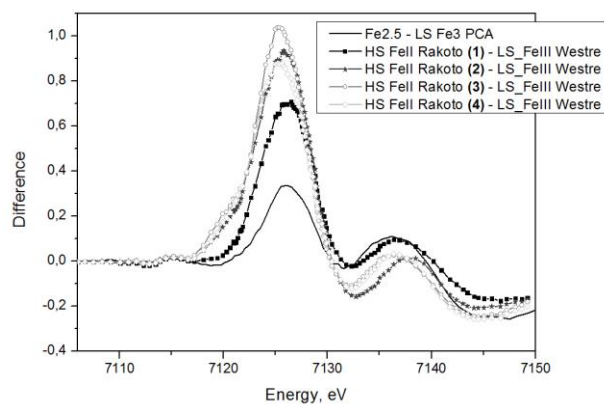


Fig. S10 Comparison of three principal components derived from the series of experimental XANES spectra with experimental spectra from ref⁵⁴ and ref⁵⁵, respectively.



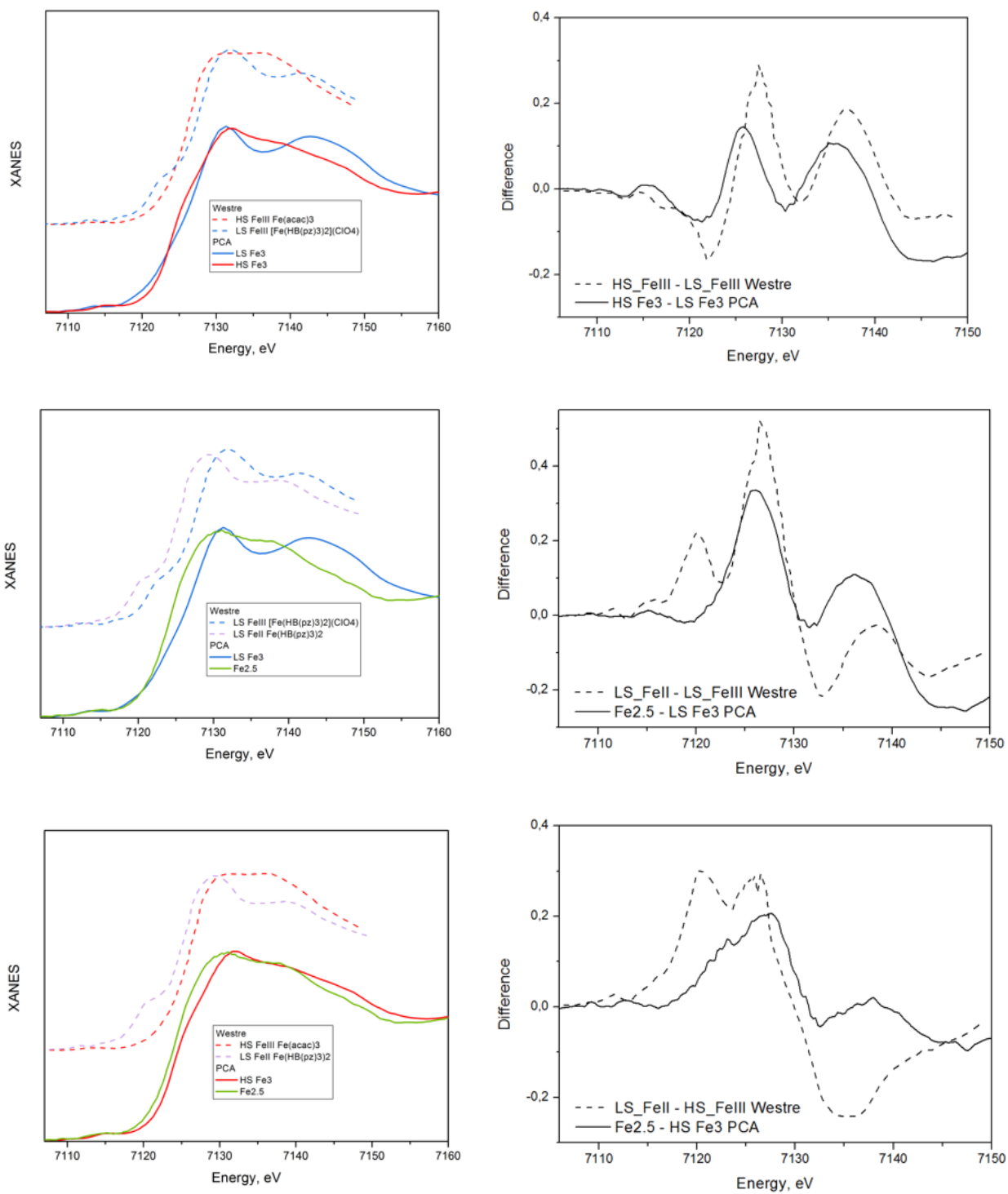


Fig. S11 Comparison of difference spectra of PCA and references

Cartesian coordinates:

Complex 1. $\Delta E_{\text{hs-ls}} = 9.4$ kcal/mol

LS-state ($E_{\text{total}} = -3816.895705$ a.u.)

15	5.623703000	0.599438000	-0.310272000
9	6.292177000	-0.540635000	0.644564000
9	4.728152000	1.142633000	0.992260000
9	4.856465000	1.733084000	-1.242619000
9	6.427875000	0.053445000	-1.607482000
9	4.367548000	-0.448613000	-0.645567000
9	6.795511000	1.655301000	0.046639000
26	-0.565589000	-0.335957000	0.315891000
8	-2.172227000	-1.161735000	-0.232047000
8	-1.525854000	1.289599000	0.062942000
7	1.106921000	0.555854000	0.934338000
7	0.444781000	-2.009237000	0.499829000
7	-1.006906000	-0.255998000	2.235866000
7	0.243027000	-0.174973000	-1.470910000
6	2.070990000	-0.487904000	1.432712000
1	3.095995000	-0.203925000	1.193652000
1	1.978528000	-0.524628000	2.523706000
6	1.726768000	-1.848552000	0.896290000
6	2.645271000	-2.894846000	0.856843000
1	3.676911000	-2.711258000	1.132856000
6	2.214546000	-4.148788000	0.434188000
1	2.911457000	-4.978358000	0.388587000
6	0.881616000	-4.318886000	0.057086000
1	0.508672000	-5.279378000	-0.278363000
6	0.029663000	-3.223707000	0.089003000
1	-1.006615000	-3.277137000	-0.222932000
6	0.688261000	1.439431000	2.055613000
1	1.546403000	1.805021000	2.630458000
1	0.160801000	2.290950000	1.618497000
6	-0.282703000	0.666945000	2.914356000
6	-0.467535000	0.883188000	4.274727000
1	0.139193000	1.618864000	4.790552000
6	-1.437615000	0.144517000	4.952270000
1	-1.601933000	0.298741000	6.012976000
6	-2.185996000	-0.794347000	4.246791000
1	-2.951002000	-1.387350000	4.733458000
6	-1.939973000	-0.969219000	2.889412000
1	-2.491485000	-1.679028000	2.285541000
6	1.657881000	1.326363000	-0.226079000
1	2.724224000	1.526350000	-0.108452000
1	1.116164000	2.276544000	-0.259398000
6	1.362151000	0.584845000	-1.501578000

6	2.135826000	0.707580000	-2.651452000
1	3.057306000	1.275807000	-2.611915000
6	1.717615000	0.057886000	-3.809573000
1	2.305769000	0.133309000	-4.717507000
6	0.546149000	-0.697781000	-3.783149000
1	0.186187000	-1.214190000	-4.665114000
6	-0.158476000	-0.802409000	-2.591258000
1	-1.065016000	-1.387555000	-2.499199000
6	-3.146115000	-0.293553000	-0.478064000
6	-4.455412000	-0.672089000	-0.882971000
6	-5.339865000	0.377655000	-1.100398000
6	-4.978088000	1.731334000	-0.940050000
6	-3.707757000	2.135998000	-0.550340000
6	-2.776364000	1.086343000	-0.312155000
6	-3.319478000	3.610259000	-0.387099000
6	-2.882534000	3.880553000	1.071313000
1	-2.030002000	3.256440000	1.343832000
1	-3.703313000	3.668015000	1.764087000
1	-2.599573000	4.932817000	1.188919000
6	-4.494733000	4.551350000	-0.705696000
1	-5.344162000	4.384224000	-0.035395000
1	-4.839255000	4.435832000	-1.738303000
1	-4.168362000	5.588436000	-0.577911000
6	-2.160438000	3.958005000	-1.349831000
1	-1.873564000	5.008498000	-1.226133000
1	-2.467468000	3.809179000	-2.389934000
1	-1.288956000	3.331164000	-1.155122000
6	-4.855202000	-2.141639000	-1.070136000
6	-6.324919000	-2.285126000	-1.504786000
1	-6.515544000	-1.791066000	-2.462710000
1	-7.011946000	-1.872597000	-0.759018000
1	-6.561026000	-3.347328000	-1.624878000
6	-4.680618000	-2.913879000	0.257712000
1	-5.302656000	-2.472837000	1.043513000
1	-3.638576000	-2.895797000	0.582791000
1	-4.985620000	-3.958656000	0.128381000
6	-3.976821000	-2.794392000	-2.162154000
1	-4.266096000	-3.842440000	-2.300946000
1	-2.921869000	-2.760056000	-1.883847000
1	-4.103494000	-2.276720000	-3.118306000
1	-5.739878000	2.476707000	-1.136273000
1	-6.356627000	0.166546000	-1.409683000

HS-state ($E_{\text{total}} = -3816.880695$ a.u.)

26	0.689549000	0.084606000	0.254574000
8	2.288995000	1.217185000	0.323446000
8	1.973455000	-1.168309000	-0.544044000

7	-1.251703000	-1.015935000	0.389700000
7	-0.592128000	1.647397000	1.059881000
7	0.808697000	-1.061601000	2.131986000
7	-0.264544000	0.541943000	-1.654764000
6	-2.168714000	-0.197993000	1.245862000
1	-3.210014000	-0.402158000	0.996235000
1	-2.005991000	-0.514341000	2.282349000
6	-1.883452000	1.283082000	1.191304000
6	-2.902496000	2.220325000	1.356900000
1	-3.930813000	1.881599000	1.414516000
6	-2.561899000	3.568906000	1.418379000
1	-3.335749000	4.318998000	1.541665000
6	-1.222332000	3.943130000	1.308363000
1	-0.920125000	4.982911000	1.352791000
6	-0.268297000	2.952119000	1.116474000
1	0.785561000	3.177009000	0.994109000
6	-0.968914000	-2.307965000	1.055807000
1	-1.889619000	-2.820746000	1.360223000
1	-0.448004000	-2.945708000	0.333759000
6	-0.054692000	-2.089513000	2.242494000
6	-0.064506000	-2.920897000	3.360583000
1	-0.783083000	-3.730385000	3.426715000
6	0.855937000	-2.690456000	4.380325000
1	0.867737000	-3.324511000	5.260239000
6	1.755294000	-1.633220000	4.256094000
1	2.486878000	-1.420065000	5.026273000
6	1.696101000	-0.840550000	3.115609000
1	2.370169000	-0.004539000	2.963723000
6	-1.799233000	-1.214890000	-0.982015000
1	-2.879211000	-1.374933000	-0.955606000
1	-1.324994000	-2.114109000	-1.390865000
6	-1.445270000	-0.061827000	-1.890758000
6	-2.262410000	0.309857000	-2.957443000
1	-3.228105000	-0.164027000	-3.084203000
6	-1.826706000	1.316273000	-3.813483000
1	-2.447923000	1.629500000	-4.645553000
6	-0.592887000	1.924258000	-3.581080000
1	-0.218995000	2.710080000	-4.226733000
6	0.153945000	1.513659000	-2.484922000
1	1.113152000	1.959733000	-2.244885000
6	3.392560000	0.633411000	-0.134074000
6	4.664634000	1.257397000	-0.152682000
6	5.705437000	0.490063000	-0.671705000
6	5.527502000	-0.821154000	-1.152389000
6	4.294540000	-1.464275000	-1.148883000
6	3.209232000	-0.711371000	-0.624174000
15	-5.833882000	-0.361537000	-0.326916000
9	-4.822128000	-1.632061000	0.059294000
9	-5.542860000	0.263218000	1.179254000

9	-7.102163000	-1.191699000	0.235756000
9	-6.759272000	0.918311000	-0.694652000
9	-6.021700000	-0.984804000	-1.821698000
9	-4.482599000	0.461847000	-0.864039000
1	6.400009000	-1.335648000	-1.537784000
1	6.704705000	0.907238000	-0.715693000
6	4.095923000	-2.891158000	-1.672769000
6	3.079739000	-2.885018000	-2.838784000
1	3.449891000	-2.271893000	-3.666860000
1	2.116444000	-2.486927000	-2.515773000
1	2.932964000	-3.905639000	-3.210545000
6	3.572640000	-3.798671000	-0.534514000
1	2.621507000	-3.428639000	-0.147903000
1	4.293355000	-3.836398000	0.289131000
1	3.428278000	-4.818986000	-0.907998000
6	5.410796000	-3.497560000	-2.193435000
1	5.218629000	-4.511648000	-2.558104000
1	6.168561000	-3.563700000	-1.405924000
1	5.824141000	-2.917359000	-3.024682000
6	4.867732000	2.687428000	0.365023000
6	6.335536000	3.136181000	0.253186000
1	6.682598000	3.135972000	-0.785036000
1	7.002265000	2.497528000	0.841483000
1	6.429069000	4.157824000	0.635336000
6	4.459970000	2.772670000	1.854485000
1	5.076800000	2.099717000	2.459459000
1	3.411070000	2.501555000	1.987674000
1	4.607547000	3.793452000	2.225294000
6	4.008383000	3.671055000	-0.462445000
1	4.140697000	4.692605000	-0.087700000
1	2.950337000	3.410179000	-0.399673000
1	4.310302000	3.653050000	-1.514703000

Complex 2. $\Delta E_{\text{HS-LS}} = 10.6$ kcal/mol

LS-state ($E_{\text{total}} = -3827.850884$ a.u.)

26	2.081499000	-0.561593000	0.016941000
8	3.942798000	-0.885929000	-0.068644000
8	2.588260000	1.273570000	0.023675000
7	0.124393000	-0.181458000	0.108666000
7	1.956253000	-0.537430000	1.977621000
7	1.566081000	-2.444773000	0.014565000
7	1.778482000	-0.472173000	-1.927093000
6	4.666090000	0.226272000	-0.060943000
6	6.087374000	0.244385000	-0.104737000
6	6.668018000	1.506642000	-0.090803000

6	5.915031000	2.698805000	-0.038831000
6	4.527343000	2.718181000	0.003403000
6	3.897264000	1.441663000	-0.008313000
6	6.916297000	-1.045691000	-0.165610000
6	6.562032000	-1.843162000	-1.441977000
6	6.633679000	-1.919062000	1.078302000
6	8.427630000	-0.754856000	-0.198611000
6	3.715407000	4.017724000	0.057479000
6	2.861181000	4.051758000	1.346035000
6	2.794110000	4.112995000	-1.180856000
6	4.624292000	5.259771000	0.064001000
6	-0.093686000	0.576638000	1.379709000
6	0.806357000	0.004846000	2.443523000
6	0.528824000	0.071557000	3.804630000
6	1.472286000	-0.412349000	4.709112000
6	2.660796000	-0.954833000	4.224715000
6	2.865173000	-1.005880000	2.851281000
6	-0.659776000	-1.467987000	0.096773000
6	0.237152000	-2.676851000	0.057117000
6	-0.278534000	-3.973351000	0.053737000
6	0.600757000	-5.049604000	0.015052000
6	1.974807000	-4.802968000	-0.023684000
6	2.419140000	-3.489720000	-0.025250000
6	-0.179360000	0.648479000	-1.095773000
6	0.605283000	0.113788000	-2.262586000
6	0.209773000	0.253069000	-3.588770000
6	1.055695000	-0.206786000	-4.596006000
6	2.267780000	-0.798279000	-4.245075000
6	2.593623000	-0.917437000	-2.899548000
1	7.747094000	1.600473000	-0.120957000
1	6.462825000	3.633862000	-0.032273000
1	7.168284000	-2.754623000	-1.495845000
1	5.507938000	-2.127658000	-1.441801000
1	6.764021000	-1.246223000	-2.337069000
1	7.234696000	-2.834842000	1.039506000
1	6.894132000	-1.379763000	1.994736000
1	5.579493000	-2.199232000	1.124026000
1	8.710700000	-0.169212000	-1.078925000
1	8.757428000	-0.217228000	0.695982000
1	8.974001000	-1.702685000	-0.238689000
1	2.178496000	3.201532000	1.384306000
1	3.502239000	4.021749000	2.233017000
1	2.273043000	4.975625000	1.380883000
1	2.108090000	3.265661000	-1.222872000
1	2.207610000	5.037728000	-1.141213000
1	3.387291000	4.124337000	-2.100921000
1	5.237444000	5.319916000	-0.841007000
1	4.001770000	6.159076000	0.105570000
1	5.287936000	5.273018000	0.934676000

1	0.218773000	1.607903000	1.193144000
1	-1.146152000	0.573399000	1.682598000
1	-0.416315000	0.488770000	4.132692000
1	1.279545000	-0.368726000	5.775525000
1	3.421890000	-1.337570000	4.894206000
1	3.766987000	-1.414335000	2.412679000
1	-1.304108000	-1.501201000	0.979670000
1	-1.335529000	-1.477734000	-0.765151000
1	-1.353052000	-4.117668000	0.067353000
1	0.221871000	-6.065802000	0.011792000
1	2.693400000	-5.613319000	-0.055685000
1	3.469285000	-3.225628000	-0.058996000
1	-1.251941000	0.690274000	-1.301288000
1	0.178263000	1.659827000	-0.884537000
1	-0.742904000	0.716486000	-3.817720000
1	0.771040000	-0.106681000	-5.637615000
1	2.955546000	-1.165039000	-4.997618000
1	3.522088000	-1.362232000	-2.563504000
6	-6.469797000	0.065206000	0.239440000
6	-7.267326000	-0.560728000	-0.741160000
6	-8.648642000	-0.714955000	-0.601269000
6	-9.293836000	-0.247648000	0.544330000
6	-8.535483000	0.372058000	1.537645000
6	-7.154981000	0.520994000	1.381468000
6	-4.122199000	0.401964000	1.496542000
6	-3.639611000	-0.706382000	2.223736000
6	-3.170960000	-0.609563000	3.538833000
6	-3.149070000	0.626401000	4.188163000
6	-3.598656000	1.753234000	3.496229000
6	-4.072278000	1.634048000	2.186889000
6	-4.261906000	-0.994600000	-0.855795000
6	-4.527473000	-2.327160000	-0.465242000
6	-4.054217000	-3.433288000	-1.174905000
6	-3.299952000	-3.254651000	-2.338589000
6	-3.047084000	-1.954944000	-2.778358000
6	-3.519749000	-0.857498000	-2.046330000
6	-4.588477000	1.673868000	-0.864619000
6	-5.523500000	2.165270000	-1.796316000
6	-5.269915000	3.279175000	-2.600975000
6	-4.056098000	3.961414000	-2.503918000
6	-3.107860000	3.513865000	-1.583147000
6	-3.380471000	2.396492000	-0.788253000
5	-4.846930000	0.292754000	0.008015000
1	-6.793134000	-0.944754000	-1.641310000
1	-9.220836000	-1.202716000	-1.386660000
1	-10.367057000	-0.367481000	0.661971000
1	-9.019034000	0.738685000	2.439781000
1	-6.596872000	1.003067000	2.179520000
1	-3.662665000	-1.690471000	1.763601000

1	-2.842853000	-1.504992000	4.062541000
1	-2.815012000	0.707159000	5.219510000
1	-3.600754000	2.724748000	3.984134000
1	-4.433780000	2.527443000	1.685513000
1	-5.161187000	-2.501816000	0.400430000
1	-4.302081000	-4.437587000	-0.838364000
1	-2.949894000	-4.110441000	-2.909026000
1	-2.500642000	-1.795992000	-3.705410000
1	-3.339201000	0.143719000	-2.431704000
1	-6.482874000	1.664340000	-1.889547000
1	-6.027413000	3.620892000	-3.301790000
1	-3.859826000	4.833252000	-3.121354000
1	-2.164633000	4.045476000	-1.473450000
1	-2.636527000	2.090616000	-0.055526000

HS-state ($E_{\text{total}} = -3827.833978$ a.u.)

6	-6.511345000	0.380959000	0.648151000
6	-7.413841000	-0.699003000	0.672094000
6	-8.727990000	-0.568312000	1.128407000
6	-9.195657000	0.664049000	1.585203000
6	-8.328362000	1.757035000	1.579122000
6	-7.016710000	1.609518000	1.121811000
6	-4.010876000	1.310107000	0.905015000
6	-3.973788000	1.297473000	2.319042000
6	-3.181237000	2.174414000	3.063553000
6	-2.401339000	3.139643000	2.419238000
6	-2.444977000	3.213391000	1.026669000
6	-3.229643000	2.312395000	0.296281000
6	-4.470578000	-1.311356000	0.222996000
6	-3.800826000	-1.812814000	1.358219000
6	-3.510129000	-3.170005000	1.536063000
6	-3.876533000	-4.100313000	0.562052000
6	-4.526530000	-3.643610000	-0.587366000
6	-4.810650000	-2.284547000	-0.744084000
6	-4.944725000	0.696413000	-1.542650000
6	-5.872933000	1.599479000	-2.095772000
6	-5.810529000	2.024740000	-3.425417000
6	-4.809204000	1.550489000	-4.273956000
6	-3.875763000	0.645147000	-3.766945000
6	-3.949089000	0.239376000	-2.430655000
5	-4.971053000	0.262198000	0.053836000
1	-7.083234000	-1.676319000	0.330782000
1	-9.387090000	-1.433040000	1.130139000
1	-10.215795000	0.769947000	1.943100000
1	-8.672046000	2.725750000	1.933485000
1	-6.362213000	2.477826000	1.139154000
1	-4.620687000	0.605544000	2.852712000
1	-3.197724000	2.129673000	4.150102000

1	-1.802509000	3.840634000	2.993697000
1	-1.884391000	3.988657000	0.508236000
1	-3.265395000	2.413669000	-0.785790000
1	-3.523039000	-1.125094000	2.152381000
1	-3.014419000	-3.502785000	2.445466000
1	-3.679737000	-5.159756000	0.704299000
1	-4.830828000	-4.350190000	-1.355736000
1	-5.331270000	-1.965909000	-1.642849000
1	-6.675431000	1.975754000	-1.467602000
1	-6.554538000	2.721017000	-3.803797000
1	-4.768317000	1.865911000	-5.312647000
1	-3.106409000	0.236261000	-4.419709000
1	-3.224575000	-0.488980000	-2.071471000
26	2.210299000	-0.389314000	-0.202637000
8	4.102960000	-0.915457000	-0.250057000
8	3.009364000	1.344432000	0.226451000
7	-0.015454000	-0.133520000	-0.228181000
7	1.573509000	-2.444161000	-0.547966000
7	1.760736000	0.250760000	-2.246059000
7	1.638642000	-0.738042000	1.880613000
6	-0.628837000	-1.399450000	-0.732802000
1	-1.611668000	-1.560218000	-0.276156000
1	-0.794811000	-1.278116000	-1.808723000
6	0.239792000	-2.625350000	-0.560198000
6	-0.326823000	-3.899170000	-0.506597000
1	-1.406578000	-4.005521000	-0.490605000
6	0.514735000	-5.007021000	-0.462330000
1	0.096581000	-6.007193000	-0.420212000
6	1.896413000	-4.815495000	-0.465622000
1	2.584209000	-5.652169000	-0.432297000
6	2.385382000	-3.516006000	-0.499364000
1	3.446448000	-3.292965000	-0.482957000
6	-0.292319000	0.977779000	-1.177161000
1	-1.355287000	1.041484000	-1.430668000
1	-0.015019000	1.911720000	-0.678392000
6	0.553422000	0.824194000	-2.419713000
6	0.134272000	1.290647000	-3.664857000
1	-0.852275000	1.728283000	-3.771044000
6	0.997277000	1.173531000	-4.751509000
1	0.694603000	1.529567000	-5.730358000
6	2.249133000	0.588090000	-4.565790000
1	2.948983000	0.478234000	-5.385595000
6	2.591302000	0.137803000	-3.296422000
1	3.551436000	-0.323936000	-3.092510000
6	-0.481718000	0.197670000	1.145956000
1	-1.544363000	-0.030537000	1.271631000
1	-0.381674000	1.278880000	1.283921000
6	0.355542000	-0.484629000	2.200080000
6	-0.151459000	-0.762395000	3.470026000

1	-1.190524000	-0.544209000	3.689440000
6	0.697014000	-1.305154000	4.429954000
1	0.325404000	-1.529097000	5.424159000
6	2.028142000	-1.557677000	4.096889000
1	2.721810000	-1.976305000	4.816304000
6	2.457466000	-1.260910000	2.810114000
1	3.480238000	-1.435469000	2.493767000
6	4.949433000	0.071187000	0.034609000
6	6.356982000	-0.083613000	0.077470000
6	7.080124000	1.063956000	0.397163000
6	6.473017000	2.305980000	0.662677000
6	5.095888000	2.495077000	0.626704000
6	4.326723000	1.344309000	0.304385000
1	7.122334000	3.139465000	0.903687000
1	8.161642000	1.016094000	0.447950000
6	4.431745000	3.846873000	0.912148000
6	3.474269000	3.719659000	2.120251000
1	4.024017000	3.409699000	3.015079000
1	2.688550000	2.988501000	1.923828000
1	3.006624000	4.688941000	2.327038000
6	3.638338000	4.313346000	-0.330709000
1	2.865090000	3.589746000	-0.593764000
1	4.306833000	4.438243000	-1.188910000
1	3.161108000	5.278608000	-0.127102000
6	5.469981000	4.932818000	1.245945000
1	4.951323000	5.876485000	1.442305000
1	6.164681000	5.101272000	0.416536000
1	6.050755000	4.679454000	2.138869000
6	7.029213000	-1.432278000	-0.212028000
6	8.562662000	-1.343952000	-0.114490000
1	8.891223000	-1.053463000	0.888529000
1	8.975129000	-0.630035000	-0.834583000
1	8.993208000	-2.326088000	-0.335112000
6	6.673539000	-1.900991000	-1.641736000
1	7.034790000	-1.179657000	-2.382057000
1	5.593649000	-2.009140000	-1.758435000
1	7.147820000	-2.867248000	-1.849143000
6	6.551479000	-2.486671000	0.812921000
1	7.022489000	-3.454499000	0.605392000
1	5.467518000	-2.608556000	0.768469000
1	6.826979000	-2.185661000	1.828946000

Complex 3. $\Delta E_{\text{hs-ls}} = 8.8$ kcal/mol

LS-state ($E_{\text{total}} = -3636.970118$ a.u.)

26	-0.190635000	-0.194782000	0.358613000
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7	1.040720000	-1.705435000	0.609157000
7	-0.629022000	-0.096509000	2.276845000
7	0.585290000	-0.004816000	-1.440029000
6	2.446109000	0.063854000	1.459984000
1	3.438649000	0.455371000	1.218800000
1	2.358128000	0.058019000	2.552163000
6	2.290249000	-1.353619000	0.983312000
6	3.348078000	-2.259411000	0.977020000
1	4.344528000	-1.907309000	1.219009000
6	3.091623000	-3.577951000	0.614402000
1	3.897649000	-4.302987000	0.590792000
6	1.792467000	-3.948925000	0.263731000
1	1.554716000	-4.966029000	-0.024985000
6	0.795969000	-2.982936000	0.257224000
1	-0.224217000	-3.193848000	-0.040014000
6	0.810685000	1.808229000	2.009516000
1	1.607425000	2.318318000	2.563160000
1	0.166284000	2.555235000	1.538741000
6	-0.036980000	0.944461000	2.910515000
6	-0.242539000	1.186808000	4.263400000
1	0.258153000	2.019362000	4.744627000
6	-1.097649000	0.348594000	4.979107000
1	-1.276327000	0.520812000	6.034732000
6	-1.713034000	-0.711682000	4.318574000
1	-2.386366000	-1.384401000	4.836062000
6	-1.451303000	-0.905313000	2.966635000
1	-1.901537000	-1.707543000	2.395279000
6	1.790997000	1.728335000	-0.271451000
1	2.834230000	2.049287000	-0.185373000
1	1.139495000	2.604932000	-0.338356000
6	1.590576000	0.897673000	-1.510395000
6	2.351660000	1.063296000	-2.662232000
1	3.194740000	1.743109000	-2.645406000
6	2.034238000	0.307759000	-3.787389000
1	2.618703000	0.410253000	-4.694818000
6	0.973337000	-0.593957000	-3.723540000
1	0.693641000	-1.198933000	-4.577869000
6	0.280711000	-0.734599000	-2.528033000
1	-0.538254000	-1.432733000	-2.408990000
6	-2.745005000	-0.530792000	-0.454767000
6	-3.984688000	-1.095558000	-0.861373000
6	-4.989644000	-0.181287000	-1.156012000
6	-4.808895000	1.213929000	-1.063491000
6	-3.612609000	1.798148000	-0.666952000
6	-2.561764000	0.891313000	-0.354144000
6	-3.420895000	3.316464000	-0.570899000

6	-3.083098000	3.710250000	0.885662000
1	-2.178133000	3.203322000	1.224413000
1	-3.903597000	3.438621000	1.557773000
1	-2.928092000	4.793043000	0.955558000
6	-4.691536000	4.082414000	-0.981299000
1	-5.540565000	3.840573000	-0.333714000
1	-4.974681000	3.872429000	-2.017655000
1	-4.504463000	5.157886000	-0.897798000
6	-2.276778000	3.764242000	-1.509990000
1	-2.133042000	4.848167000	-1.433969000
1	-2.518817000	3.525176000	-2.550455000
1	-1.341077000	3.266459000	-1.251333000
6	-4.189999000	-2.612609000	-0.972055000
6	-5.620688000	-2.965791000	-1.416799000
1	-5.851520000	-2.555374000	-2.404830000
1	-6.368700000	-2.600172000	-0.706160000
1	-5.720335000	-4.054503000	-1.476186000
6	-3.942418000	-3.285118000	0.397726000
1	-4.634039000	-2.892908000	1.150544000
1	-2.919052000	-3.109548000	0.734599000
1	-4.102010000	-4.366545000	0.318575000
6	-3.213395000	-3.203453000	-2.014891000
1	-3.370913000	-4.284144000	-2.107957000
1	-2.177216000	-3.029415000	-1.718570000
1	-3.378013000	-2.749042000	-2.997104000
1	-5.652222000	1.844205000	-1.319979000
1	-5.961497000	-0.537483000	-1.476202000
17	5.644160000	0.641891000	-0.535447000
8	7.052414000	0.769607000	-0.962768000
8	5.567467000	0.236430000	0.917076000
8	4.927321000	1.962022000	-0.689910000
8	4.921155000	-0.386064000	-1.353533000

HS-state ($E_{\text{total}} = -3636.956156$ a.u.)

26	0.331335000	0.122647000	0.265942000
8	1.969868000	1.199309000	0.286657000
8	1.556346000	-1.192360000	-0.519625000
7	-1.637511000	-0.905259000	0.467291000
7	-0.883094000	1.759173000	1.046627000
7	0.441362000	-0.966525000	2.182760000
7	-0.654782000	0.582934000	-1.634053000
6	-2.527626000	-0.020926000	1.284329000
1	-3.576754000	-0.205259000	1.040403000
1	-2.377469000	-0.298890000	2.333889000
6	-2.188805000	1.444404000	1.170336000
6	-3.176055000	2.423295000	1.274998000
1	-4.217043000	2.122568000	1.309341000

6	-2.789761000	3.760942000	1.292231000
1	-3.538495000	4.542248000	1.368420000
6	-1.435905000	4.083574000	1.197309000
1	-1.097465000	5.113021000	1.209153000
6	-0.514715000	3.052518000	1.059021000
1	0.547860000	3.236336000	0.943139000
6	-1.406318000	-2.178784000	1.185986000
1	-2.347035000	-2.630609000	1.522061000
1	-0.928999000	-2.873198000	0.486300000
6	-0.463327000	-1.951130000	2.347793000
6	-0.490211000	-2.735094000	3.499644000
1	-1.241486000	-3.509496000	3.608742000
6	0.455365000	-2.503711000	4.495724000
1	0.454303000	-3.101423000	5.400835000
6	1.397003000	-1.492257000	4.315007000
1	2.149695000	-1.279948000	5.064856000
6	1.353473000	-0.745217000	3.143414000
1	2.060723000	0.053337000	2.947062000
6	-2.188016000	-1.140887000	-0.897191000
1	-3.261468000	-1.342455000	-0.868936000
1	-1.687461000	-2.031674000	-1.293464000
6	-1.861387000	0.009006000	-1.817700000
6	-2.725866000	0.406603000	-2.836162000
1	-3.709312000	-0.048228000	-2.903674000
6	-2.305192000	1.406799000	-3.709107000
1	-2.958740000	1.740731000	-4.507893000
6	-1.044292000	1.978361000	-3.539308000
1	-0.680963000	2.754800000	-4.202342000
6	-0.253880000	1.545734000	-2.481520000
1	0.726531000	1.968525000	-2.289257000
6	3.043993000	0.567552000	-0.178052000
6	4.335628000	1.147456000	-0.236655000
6	5.340273000	0.331466000	-0.752802000
6	5.109716000	-0.985740000	-1.192474000
6	3.855991000	-1.586378000	-1.149684000
6	2.805995000	-0.781588000	-0.630227000
1	5.957523000	-1.540088000	-1.577747000
1	6.351932000	0.712954000	-0.827099000
6	3.600783000	-3.021230000	-1.625198000
6	2.567347000	-3.017984000	-2.775733000
1	2.943624000	-2.442769000	-3.627920000
1	1.622167000	-2.579555000	-2.451477000
1	2.382357000	-4.044287000	-3.113246000
6	3.065671000	-3.873652000	-0.450273000
1	2.133372000	-3.460346000	-0.061632000
1	3.797897000	-3.908995000	0.363254000
1	2.881556000	-4.900094000	-0.787828000
6	4.886385000	-3.688637000	-2.143956000
1	4.654074000	-4.706172000	-2.473966000

1	5.652261000	-3.756969000	-1.364491000
1	5.308159000	-3.149046000	-2.998053000
6	4.595802000	2.583716000	0.237191000
6	6.073875000	2.981729000	0.079223000
1	6.395792000	2.940794000	-0.966240000
1	6.733876000	2.338644000	0.670263000
1	6.208402000	4.010231000	0.429747000
6	4.224869000	2.720326000	1.732034000
1	4.835703000	2.045896000	2.341420000
1	3.171945000	2.482160000	1.893525000
1	4.409327000	3.745909000	2.072212000
6	3.748591000	3.571506000	-0.597826000
1	3.922711000	4.598391000	-0.256122000
1	2.684791000	3.346440000	-0.502668000
1	4.023863000	3.513923000	-1.655942000
17	-5.910440000	-0.649054000	-0.482785000
8	-5.411863000	0.734933000	-0.148032000
8	-5.203956000	-1.625560000	0.428087000
8	-7.372583000	-0.734337000	-0.299669000
8	-5.528215000	-0.963888000	-1.900218000

Complex 4. $\Delta E_{\text{hs-ls}} = 9.6$ kcal/mol

LS-state ($E_{\text{total}} = -3300.688381$ a.u.)

26	-0.045206000	-0.344708000	0.239975000
8	-1.700039000	-1.151026000	-0.183959000
8	-0.998390000	1.290996000	0.045920000
7	1.680957000	0.530427000	0.718301000
7	0.941087000	-2.031621000	0.376117000
7	-0.327962000	-0.264729000	2.188110000
7	0.645133000	-0.214917000	-1.605096000
6	2.705747000	-0.518040000	1.065014000
1	3.675105000	-0.269694000	0.625951000
1	2.836996000	-0.514080000	2.152064000
6	2.255995000	-1.891203000	0.651204000
6	3.135979000	-2.970959000	0.588907000
1	4.192149000	-2.806694000	0.769050000
6	2.635291000	-4.229954000	0.274031000
1	3.300777000	-5.084398000	0.216947000
6	1.269905000	-4.374824000	0.021052000
1	0.841139000	-5.338283000	-0.228007000
6	0.456668000	-3.251687000	0.068293000
1	-0.604327000	-3.285984000	-0.148383000
6	1.394355000	1.386837000	1.899841000
1	2.314700000	1.714087000	2.394205000
1	0.853564000	2.265870000	1.539413000

6	0.482974000	0.616782000	2.821963000
6	0.422215000	0.801829000	4.198586000
1	1.095497000	1.504135000	4.676919000
6	-0.511079000	0.077065000	4.939511000
1	-0.578054000	0.207978000	6.013938000
6	-1.350708000	-0.816630000	4.279372000
1	-2.092521000	-1.395945000	4.815909000
6	-1.227162000	-0.963544000	2.902508000
1	-1.852853000	-1.638259000	2.331426000
6	2.088280000	1.337050000	-0.474396000
1	3.139181000	1.627449000	-0.431809000
1	1.464233000	2.236046000	-0.469891000
6	1.753588000	0.556546000	-1.713013000
6	2.478824000	0.644625000	-2.896830000
1	3.395822000	1.223304000	-2.909181000
6	2.014605000	-0.046807000	-4.013922000
1	2.560148000	0.001864000	-4.950020000
6	0.850559000	-0.807227000	-3.911030000
1	0.454904000	-1.352504000	-4.759797000
6	0.199461000	-0.879497000	-2.685440000
1	-0.697244000	-1.468564000	-2.536398000
6	-2.676592000	-0.269438000	-0.366994000
6	-4.016230000	-0.629758000	-0.677183000
6	-4.898493000	0.432299000	-0.838002000
6	-4.506512000	1.780680000	-0.710454000
6	-3.206177000	2.167840000	-0.412411000
6	-2.275869000	1.105172000	-0.235956000
6	-2.785932000	3.636785000	-0.284458000
6	-2.241228000	3.906095000	1.137345000
1	-1.382826000	3.267873000	1.351966000
1	-3.014073000	3.711708000	1.888207000
1	-1.932166000	4.953633000	1.227611000
6	-3.967690000	4.594313000	-0.521348000
1	-4.768040000	4.443543000	0.210438000
1	-4.388623000	4.479847000	-1.525371000
1	-3.616957000	5.626738000	-0.423304000
6	-1.695696000	3.965159000	-1.330577000
1	-1.385783000	5.011760000	-1.232382000
1	-2.080161000	3.817432000	-2.344837000
1	-0.820864000	3.327195000	-1.197433000
6	-4.450074000	-2.093900000	-0.828662000
6	-5.947918000	-2.216236000	-1.161531000
1	-6.195710000	-1.721446000	-2.105884000
1	-6.575676000	-1.790382000	-0.372299000
1	-6.208566000	-3.274910000	-1.261256000
6	-4.197094000	-2.863610000	0.488000000
1	-4.757644000	-2.410846000	1.312441000
1	-3.135236000	-2.859622000	0.741277000
1	-4.525140000	-3.904227000	0.384245000

6	-3.657262000	-2.764303000	-1.974224000
1	-3.968690000	-3.809283000	-2.085976000
1	-2.585376000	-2.741245000	-1.768624000
1	-3.842606000	-2.250352000	-2.922825000
1	-5.268724000	2.536670000	-0.857773000
1	-5.937187000	0.235275000	-1.075346000
5	5.674950000	1.103609000	-0.387781000
9	5.005831000	1.558952000	0.795883000
9	5.349362000	-0.281176000	-0.544786000
9	5.127678000	1.812355000	-1.493030000
9	7.040240000	1.286094000	-0.289017000

HS-state ($E_{\text{total}} = -3300.673143$ a.u.)

26	0.158681000	0.092841000	0.193937000
8	1.756214000	1.215928000	0.380375000
8	1.475658000	-1.134054000	-0.589714000
7	-1.771276000	-1.020274000	0.222449000
7	-1.173060000	1.635362000	0.971704000
7	0.209772000	-1.107333000	2.039942000
7	-0.722584000	0.610746000	-1.739595000
6	-2.722994000	-0.235253000	1.070616000
1	-3.756108000	-0.461439000	0.805088000
1	-2.571604000	-0.560060000	2.106227000
6	-2.464084000	1.249935000	1.038033000
6	-3.506222000	2.168978000	1.156016000
1	-4.529589000	1.807377000	1.164410000
6	-3.190037000	3.522812000	1.241557000
1	-3.980297000	4.260639000	1.331270000
6	-1.852855000	3.918843000	1.201316000
1	-1.569893000	4.962884000	1.268052000
6	-0.874087000	2.944171000	1.051977000
1	0.180654000	3.188219000	0.985309000
6	-1.513294000	-2.333364000	0.856845000
1	-2.446001000	-2.851929000	1.109253000
1	-0.965888000	-2.948671000	0.134909000
6	-0.643312000	-2.149087000	2.082157000
6	-0.682688000	-3.018664000	3.170411000
1	-1.392736000	-3.838223000	3.181495000
6	0.195633000	-2.811363000	4.231505000
1	0.183286000	-3.475221000	5.089192000
6	1.083328000	-1.738226000	4.178089000
1	1.781679000	-1.541892000	4.982823000
6	1.055770000	-0.907973000	3.063680000
1	1.722181000	-0.057858000	2.966063000
6	-2.272419000	-1.172409000	-1.172698000
1	-3.351458000	-1.345594000	-1.186667000
1	-1.771751000	-2.048198000	-1.600751000
6	-1.901229000	0.020365000	-2.020478000

6	-2.702356000	0.443154000	-3.080292000
1	-3.671800000	-0.015984000	-3.229660000
6	-2.248491000	1.481095000	-3.888517000
1	-2.855628000	1.832934000	-4.715698000
6	-1.014323000	2.070732000	-3.614430000
1	-0.625443000	2.879137000	-4.222349000
6	-0.287535000	1.613149000	-2.522818000
1	0.668223000	2.047268000	-2.248902000
6	2.879658000	0.641140000	-0.038572000
6	4.154423000	1.254970000	0.036574000
6	5.217765000	0.500408000	-0.455121000
6	5.058472000	-0.789269000	-0.996650000
6	3.823394000	-1.422230000	-1.085111000
6	2.715840000	-0.682917000	-0.588419000
1	5.947350000	-1.295001000	-1.355287000
1	6.220421000	0.911051000	-0.428338000
6	3.644179000	-2.823720000	-1.679782000
6	2.695444000	-2.756279000	-2.899564000
1	3.117425000	-2.113022000	-3.678609000
1	1.719401000	-2.360692000	-2.613772000
1	2.559764000	-3.758608000	-3.321986000
6	3.049684000	-3.774281000	-0.614186000
1	2.078951000	-3.413811000	-0.269937000
1	3.719777000	-3.851574000	0.248455000
1	2.923274000	-4.777062000	-1.038357000
6	4.981470000	-3.421040000	-2.151777000
1	4.802054000	-4.417503000	-2.568116000
1	5.693503000	-3.526834000	-1.326793000
1	5.445165000	-2.811735000	-2.934268000
6	4.336320000	2.662080000	0.619679000
6	5.810602000	3.103951000	0.606619000
1	6.216280000	3.139463000	-0.409547000
1	6.439351000	2.439037000	1.207616000
1	5.888149000	4.110111000	1.031112000
6	3.848613000	2.693195000	2.086981000
1	4.425712000	1.990204000	2.697100000
1	2.791636000	2.428659000	2.152677000
1	3.984386000	3.696805000	2.506052000
6	3.528677000	3.682671000	-0.215177000
1	3.645220000	4.688352000	0.205150000
1	2.467616000	3.426160000	-0.220864000
1	3.888252000	3.702212000	-1.249140000
5	-5.942198000	-0.676536000	-0.358095000
9	-5.954267000	0.072842000	0.851311000
9	-7.221108000	-0.939499000	-0.808892000
9	-5.196779000	0.069687000	-1.324962000
9	-5.217982000	-1.888443000	-0.117751000