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**Supporting information for article:**

# Alternative difference analysis scheme combining *R*-space EXAFS fit with global optimization XANES fit for X-ray transient absorption spectroscopy

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**Supporting information**

**Table .S0 fit results with FEFF calculation and various optimization algorithms.**

| Search method | Bond length change Å | Fraction | R factor | Structure | Picture of fit result | Number of FEFF calculations |
|---|---|---|---|---|---|---|
| 1Direct_L | 0.119 | 36% | 0.00596 | Table.S1 | Fig.S1 | 157 |
| 2Direct_L Bound | 0.116 | 37% | 0.00596 | Table.S2 | Fig.S2 | 107 |
| 3CRS | 0.107 | 38% | 0.00662 | Table.S3 | Fig.S3 | 382 |
| 4ISRES | 0.087 | 45% | 0.00659 | Table.S4 | Fig.S4 | 1051 |
| 5ESCH | 0.040 | 89% | 0.00619 | Table.S5 | Fig.S5 | 1992 |
| 6BOBYQA | 0.038 | 90% | 0.00660 | Table.S6 | Fig.S6 | 22 |
| 7COBYLA | 0.041 | 86% | 0.00621 | Table.S7 | Fig.S7 | 91 |
| 8SBPLX | 0.067 | 56% | 0.00624 | Table.S8 | Fig.S8 | 210 |

In “Direct_L Bound” , we used [-0.05Å,0.3Å] boundary limitation of bond length change, while in other fit, we used [-0.3Å,0.3Å] boundary limitation of bond length change. R factors of ISRES and Direct_L algorithms are improved compared to previous data in paper. Beyond deterministic global optimization algorithms Direct, heuristics and stochastic global optimization algorithms CRS, ISRES, ESCH, we also added local optimization algorithms such as BOBYQA, COBYLA, SPBLX. Generally, local algorithms use less calculation cycles than global ones. Among them, the deterministic global

optimization algorithms Direct reaches the best objective function value within comparative calculation cycles to local algorithms.

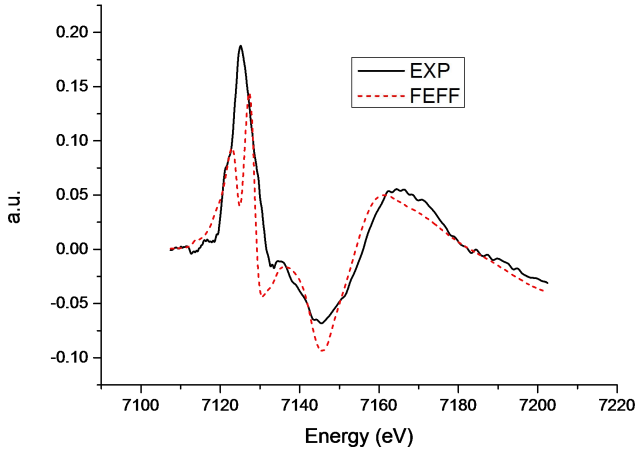



**Figure S1. Experimental difference XANES (EXP) and fit result (FEFF) of HS state (FEFF calculation with DIRECT_L optimization algorithm).**

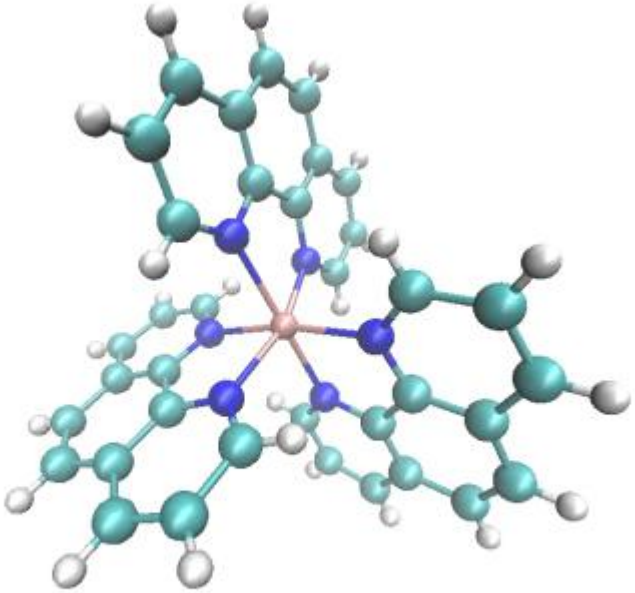


**Table S1. Fit result of HS state (FEFF with DIRECT_L)**

The coordinates of atoms in Fe(II)(phen)$_3$ complex for HS state with best fit in unit Å

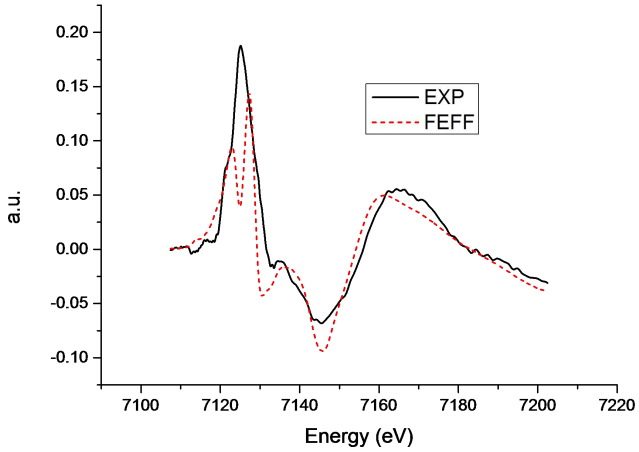
| | | | |
|---|---|---|---|
| Fe | 0.000000 | 0.000000 | 0.000000 |
| N | 0.437000 | 0.115000 | 2.023000 |
| N | -1.120000 | -1.720000 | -0.095000 |
| N | 1.372000 | -1.490000 | -0.792000 |
| N | 1.153000 | 1.615000 | -0.530000 |
| N | -1.397000 | 1.374000 | 0.670000 |
| N | -0.495000 | 0.258000 | -2.023000 |
| C | -1.234000 | 1.776000 | 1.966000 |
| C | -0.249000 | 1.077000 | 2.708000 |
| C | -0.442000 | -2.899000 | -0.267000 |
| C | 1.339000 | -0.590000 | 2.699000 |

| | | | |
|---|---|---|---|
| H | 1.820000 | -1.270000 | 2.243000 |
| C | 0.928000 | -2.764000 | -0.659000 |
| C | 0.183000 | 1.257000 | -2.649000 |
| C | 1.075000 | 2.008000 | -1.835000 |
| C | -1.351000 | -0.468000 | -2.753000 |
| H | -1.837000 | -1.172000 | -2.337000 |
| C | -2.413000 | -1.805000 | 0.269000 |
| H | -2.914000 | -1.008000 | 0.384000 |
| C | -2.349000 | 1.970000 | -0.036000 |
| H | -2.501000 | 1.689000 | -0.931000 |
| C | 1.972000 | 2.318000 | 0.268000 |
| H | 2.055000 | 2.058000 | 1.177000 |
| C | 2.651000 | -1.336000 | -1.172000 |
| H | 2.992000 | -0.455000 | -1.272000 |
| C | -0.026000 | 1.381000 | 4.057000 |
| C | 2.712000 | 3.417000 | -0.186000 |
| H | 3.262000 | 3.902000 | 0.417000 |
| C | 0.041000 | 1.573000 | -4.005000 |
| C | 1.799000 | 3.082000 | -2.370000 |
| C | -1.001000 | -4.161000 | -0.080000 |
| C | -1.977000 | 2.806000 | 2.564000 |
| C | 1.612000 | -0.369000 | 4.060000 |
| H | 2.257000 | -0.900000 | 4.512000 |
| C | -3.144000 | 3.003000 | 0.491000 |
| H | -3.813000 | 3.409000 | -0.048000 |
| C | 3.496000 | -2.414000 | -1.421000 |

| | | | |
|---|---|---|---|
| H | 4.392000 | -2.260000 | -1.698000 |
| C | 1.712000 | -3.898000 | -0.877000 |
| C | -3.034000 | -3.035000 | 0.481000 |
| H | -3.945000 | -3.059000 | 0.748000 |
| C | -1.546000 | -0.213000 | -4.118000 |
| H | -2.160000 | -0.743000 | -4.611000 |
| C | 3.043000 | -3.677000 | -1.272000 |
| H | 3.623000 | -4.413000 | -1.431000 |
| C | 0.939000 | 0.623000 | 4.732000 |
| H | 1.126000 | 0.794000 | 5.649000 |
| C | -2.956000 | 3.423000 | 1.774000 |
| H | -3.485000 | 4.128000 | 2.129000 |
| C | -0.782000 | 2.445000 | 4.647000 |
| H | -0.631000 | 2.677000 | 5.557000 |
| C | -2.352000 | -4.205000 | 0.313000 |
| H | -2.783000 | -5.039000 | 0.458000 |
| C | 1.632000 | 3.375000 | -3.765000 |
| H | 2.124000 | 4.090000 | -4.154000 |
| C | -1.704000 | 3.122000 | 3.932000 |
| H | -2.185000 | 3.827000 | 4.349000 |
| C | 0.791000 | 2.656000 | -4.530000 |
| H | 0.698000 | 2.879000 | -5.448000 |
| C | -0.864000 | 0.784000 | -4.743000 |
| H | -0.998000 | 0.949000 | -5.670000 |
| C | 2.638000 | 3.786000 | -1.492000 |
| H | 3.153000 | 4.519000 | -1.809000 |

| | | | |
|---|---|---|---|
| C | 1.118000 | -5.171000 | -0.674000 |
| H | 1.646000 | -5.949000 | -0.811000 |
| C | -0.171000 | -5.314000 | -0.293000 |
| H | -0.532000 | -6.185000 | -0.165000 |

**Figure S2. Experimental difference XANES (EXP) and fit result (FEFF) of HS state (FEFF calculation with DIRECT_L optimization algorithm and boundary limitation of bound length change).**



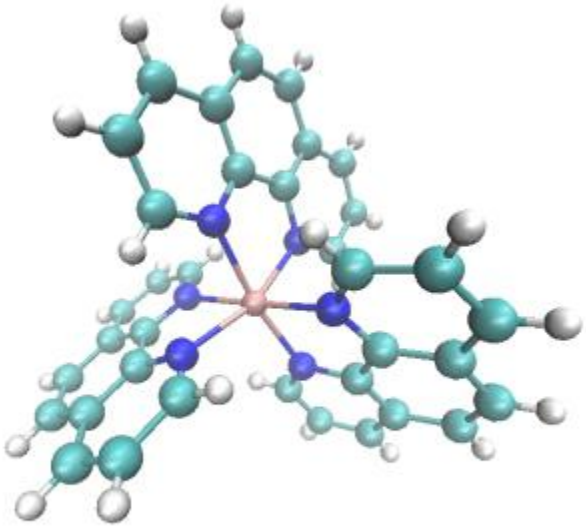



**Table S2. Fit result of HS state (FEFF with DIRECT_L and and boundary limitation of bound length change)**

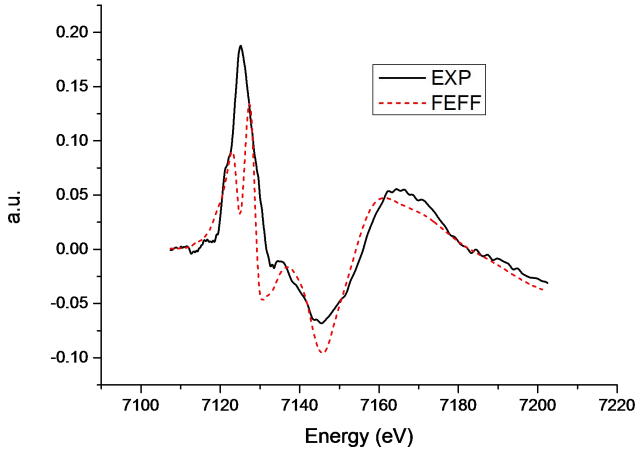
The coordinates of atoms in Fe(II)$(phen)_3$ complex for HS state with best fit in unit Å

| | | | |
|---|---|---|---|
| Fe | 0.000000 | 0.000000 | 0.000000 |
| N | 0.440000 | 0.111000 | 2.016000 |
| N | -1.120000 | -1.723000 | -0.095000 |
| N | 1.372000 | -1.493000 | -0.792000 |
| N | 1.151000 | 1.611000 | -0.524000 |
| N | -1.394000 | 1.370000 | 0.663000 |
| N | -0.497000 | 0.254000 | -2.017000 |
| C | -1.231000 | 1.772000 | 1.959000 |
| C | -0.246000 | 1.073000 | 2.701000 |
| C | -0.442000 | -2.902000 | -0.267000 |
| C | 1.342000 | -0.594000 | 2.692000 |
| H | 1.823000 | -1.274000 | 2.236000 |
| C | 0.928000 | -2.767000 | -0.659000 |
| C | 0.181000 | 1.253000 | -2.643000 |
| C | 1.073000 | 2.004000 | -1.829000 |
| C | -1.353000 | -0.472000 | -2.747000 |
| H | -1.839000 | -1.176000 | -2.331000 |
| C | -2.413000 | -1.808000 | 0.269000 |
| H | -2.914000 | -1.011000 | 0.384000 |
| C | -2.346000 | 1.966000 | -0.043000 |
| H | -2.498000 | 1.685000 | -0.938000 |

| | | | |
|---|---|---|---|
| C | 1.970000 | 2.314000 | 0.274000 |
| H | 2.053000 | 2.054000 | 1.183000 |
| C | 2.651000 | -1.339000 | -1.172000 |
| H | 2.992000 | -0.458000 | -1.272000 |
| C | -0.023000 | 1.377000 | 4.050000 |
| C | 2.710000 | 3.413000 | -0.180000 |
| H | 3.260000 | 3.898000 | 0.423000 |
| C | 0.039000 | 1.569000 | -3.999000 |
| C | 1.797000 | 3.078000 | -2.364000 |
| C | -1.001000 | -4.164000 | -0.080000 |
| C | -1.974000 | 2.802000 | 2.557000 |
| C | 1.615000 | -0.373000 | 4.053000 |
| H | 2.260000 | -0.904000 | 4.505000 |
| C | -3.141000 | 2.999000 | 0.484000 |
| H | -3.810000 | 3.405000 | -0.055000 |
| C | 3.496000 | -2.417000 | -1.421000 |
| H | 4.392000 | -2.263000 | -1.698000 |
| C | 1.712000 | -3.901000 | -0.877000 |
| C | -3.034000 | -3.038000 | 0.481000 |
| H | -3.945000 | -3.062000 | 0.748000 |
| C | -1.548000 | -0.217000 | -4.112000 |
| H | -2.162000 | -0.747000 | -4.605000 |
| C | 3.043000 | -3.680000 | -1.272000 |
| H | 3.623000 | -4.416000 | -1.431000 |
| C | 0.942000 | 0.619000 | 4.725000 |
| H | 1.129000 | 0.790000 | 5.642000 |

| | | | |
|---|---|---|---|
| C | -2.953000 | 3.419000 | 1.767000 |
| H | -3.482000 | 4.124000 | 2.122000 |
| C | -0.779000 | 2.441000 | 4.640000 |
| H | -0.628000 | 2.673000 | 5.550000 |
| C | -2.352000 | -4.208000 | 0.313000 |
| H | -2.783000 | -5.042000 | 0.458000 |
| C | 1.630000 | 3.371000 | -3.759000 |
| H | 2.122000 | 4.086000 | -4.148000 |
| C | -1.701000 | 3.118000 | 3.925000 |
| H | -2.182000 | 3.823000 | 4.342000 |
| C | 0.789000 | 2.652000 | -4.524000 |
| H | 0.696000 | 2.875000 | -5.442000 |
| C | -0.866000 | 0.780000 | -4.737000 |
| H | -1.000000 | 0.945000 | -5.664000 |
| C | 2.636000 | 3.782000 | -1.486000 |
| H | 3.151000 | 4.515000 | -1.803000 |
| C | 1.118000 | -5.174000 | -0.674000 |
| H | 1.646000 | -5.952000 | -0.811000 |
| C | -0.171000 | -5.317000 | -0.293000 |
| H | -0.532000 | -6.188000 | -0.165000 |

**Figure S3. Experimental difference XANES (EXP) and fit result (FEFF) of HS state (FEFF calculation with CRS optimization algorithm).**



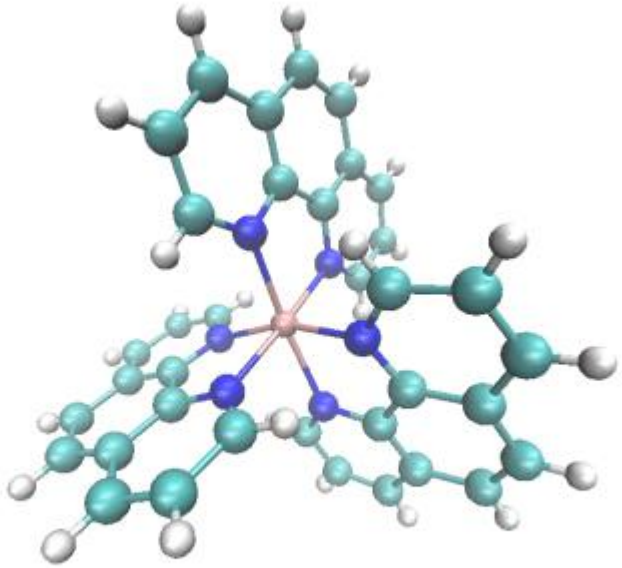



**Table S3. Fit result of HS state (FEFF with CRS)**

The coordinates of atoms in Fe(II)(phen)$_3$ complex for HS state with best fit in unit Å

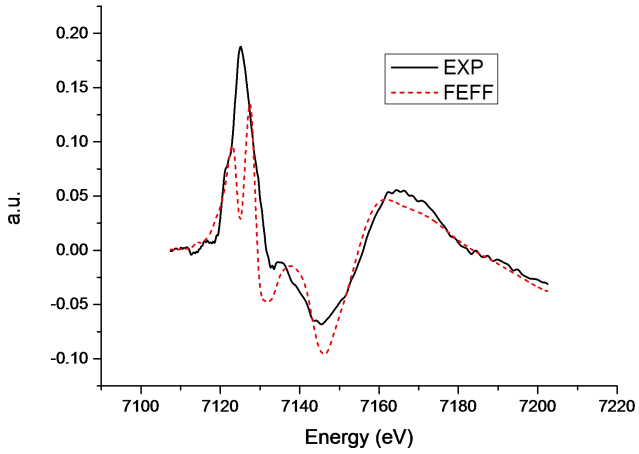
| | | | |
|---|---|---|---|
| Fe | 0.000000 | 0.000000 | 0.000000 |
| N | 0.606000 | 0.206000 | 2.035000 |
| N | -1.130000 | -1.670000 | 0.155000 |
| N | 1.362000 | -1.440000 | -0.542000 |

| | | | |
|---|---|---|---|
| N | 1.457000 | 1.354000 | -0.629000 |
| N | -1.228000 | 1.465000 | 0.682000 |
| N | -0.191000 | -0.003000 | -2.122000 |
| C | -1.065000 | 1.867000 | 1.978000 |
| C | -0.080000 | 1.168000 | 2.720000 |
| C | -0.452000 | -2.849000 | -0.017000 |
| C | 1.508000 | -0.499000 | 2.711000 |
| H | 1.989000 | -1.179000 | 2.255000 |
| C | 0.918000 | -2.714000 | -0.409000 |
| C | 0.487000 | 0.996000 | -2.748000 |
| C | 1.379000 | 1.747000 | -1.934000 |
| C | -1.047000 | -0.729000 | -2.852000 |
| H | -1.533000 | -1.433000 | -2.436000 |
| C | -2.423000 | -1.755000 | 0.519000 |
| H | -2.924000 | -0.958000 | 0.634000 |
| C | -2.180000 | 2.061000 | -0.024000 |
| H | -2.332000 | 1.780000 | -0.919000 |
| C | 2.276000 | 2.057000 | 0.169000 |
| H | 2.359000 | 1.797000 | 1.078000 |
| C | 2.641000 | -1.286000 | -0.922000 |
| H | 2.982000 | -0.405000 | -1.022000 |
| C | 0.143000 | 1.472000 | 4.069000 |
| C | 3.016000 | 3.156000 | -0.285000 |
| H | 3.566000 | 3.641000 | 0.318000 |
| C | 0.345000 | 1.312000 | -4.104000 |
| C | 2.103000 | 2.821000 | -2.469000 |

| | | | |
|---|---|---|---|
| C | -1.011000 | -4.111000 | 0.170000 |
| C | -1.808000 | 2.897000 | 2.576000 |
| C | 1.781000 | -0.278000 | 4.072000 |
| H | 2.426000 | -0.809000 | 4.524000 |
| C | -2.975000 | 3.094000 | 0.503000 |
| H | -3.644000 | 3.500000 | -0.036000 |
| C | 3.486000 | -2.364000 | -1.171000 |
| H | 4.382000 | -2.210000 | -1.448000 |
| C | 1.702000 | -3.848000 | -0.627000 |
| C | -3.044000 | -2.985000 | 0.731000 |
| H | -3.955000 | -3.009000 | 0.998000 |
| C | -1.242000 | -0.474000 | -4.217000 |
| H | -1.856000 | -1.004000 | -4.710000 |
| C | 3.033000 | -3.627000 | -1.022000 |
| H | 3.613000 | -4.363000 | -1.181000 |
| C | 1.108000 | 0.714000 | 4.744000 |
| H | 1.295000 | 0.885000 | 5.661000 |
| C | -2.787000 | 3.514000 | 1.786000 |
| H | -3.316000 | 4.219000 | 2.141000 |
| C | -0.613000 | 2.536000 | 4.659000 |
| H | -0.462000 | 2.768000 | 5.569000 |
| C | -2.362000 | -4.155000 | 0.563000 |
| H | -2.793000 | -4.989000 | 0.708000 |
| C | 1.936000 | 3.114000 | -3.864000 |
| H | 2.428000 | 3.829000 | -4.253000 |
| C | -1.535000 | 3.213000 | 3.944000 |

| | | | |
|---|---|---|---|
| H | -2.016000 | 3.918000 | 4.361000 |
| C | 1.095000 | 2.395000 | -4.629000 |
| H | 1.002000 | 2.618000 | -5.547000 |
| C | -0.560000 | 0.523000 | -4.842000 |
| H | -0.694000 | 0.688000 | -5.769000 |
| C | 2.942000 | 3.525000 | -1.591000 |
| H | 3.457000 | 4.258000 | -1.908000 |
| C | 1.108000 | -5.121000 | -0.424000 |
| H | 1.636000 | -5.899000 | -0.561000 |
| C | -0.181000 | -5.264000 | -0.043000 |
| H | -0.542000 | -6.135000 | 0.085000 |

**Figure S4. Experimental difference XANES (EXP) and fit result (FEFF) of HS state (FEFF calculation with ISRES optimization algorithm).**



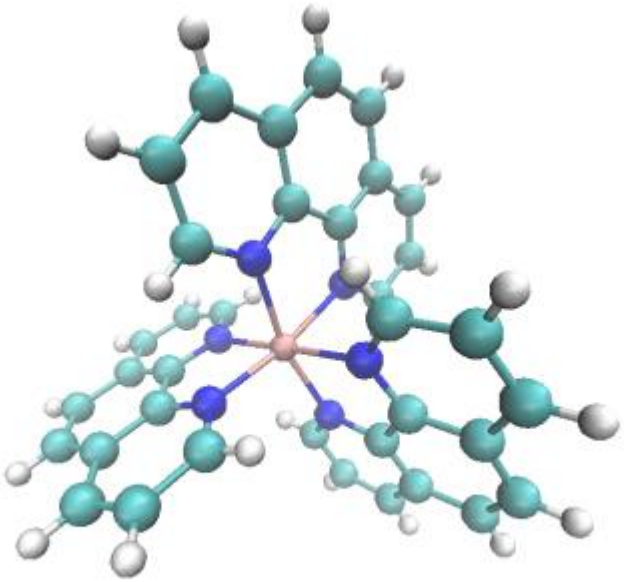


**Table S4. Fit result of HS state (FEFF with ISRES)**

The coordinates of atoms in Fe(II)(phen)$_3$ complex for HS state with best fit in unit Å

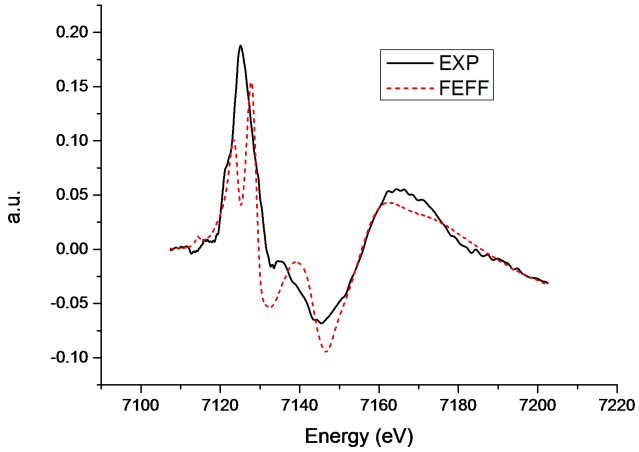
| | | | |
|---|---|---|---|
| Fe | 0.000000 | 0.000000 | 0.000000 |
| N | 0.598000 | 0.293000 | 1.965000 |
| N | -1.167000 | -1.699000 | 0.451000 |
| N | 1.325000 | -1.469000 | -0.246000 |
| N | 1.174000 | 1.613000 | -0.467000 |
| N | -1.236000 | 1.552000 | 0.612000 |
| N | -0.474000 | 0.256000 | -1.960000 |
| C | -1.073000 | 1.954000 | 1.908000 |
| C | -0.088000 | 1.255000 | 2.650000 |
| C | -0.489000 | -2.878000 | 0.279000 |
| C | 1.500000 | -0.412000 | 2.641000 |

| | | | |
|---|---|---|---|
| H | 1.981000 | -1.092000 | 2.185000 |
| C | 0.881000 | -2.743000 | -0.113000 |
| C | 0.204000 | 1.255000 | -2.586000 |
| C | 1.096000 | 2.006000 | -1.772000 |
| C | -1.330000 | -0.470000 | -2.690000 |
| H | -1.816000 | -1.174000 | -2.274000 |
| C | -2.460000 | -1.784000 | 0.815000 |
| H | -2.961000 | -0.987000 | 0.930000 |
| C | -2.188000 | 2.148000 | -0.094000 |
| H | -2.340000 | 1.867000 | -0.989000 |
| C | 1.993000 | 2.316000 | 0.331000 |
| H | 2.076000 | 2.056000 | 1.240000 |
| C | 2.604000 | -1.315000 | -0.626000 |
| H | 2.945000 | -0.434000 | -0.726000 |
| C | 0.135000 | 1.559000 | 3.999000 |
| C | 2.733000 | 3.415000 | -0.123000 |
| H | 3.283000 | 3.900000 | 0.480000 |
| C | 0.062000 | 1.571000 | -3.942000 |
| C | 1.820000 | 3.080000 | -2.307000 |
| C | -1.048000 | -4.140000 | 0.466000 |
| C | -1.816000 | 2.984000 | 2.506000 |
| C | 1.773000 | -0.191000 | 4.002000 |
| H | 2.418000 | -0.722000 | 4.454000 |
| C | -2.983000 | 3.181000 | 0.433000 |
| H | -3.652000 | 3.587000 | -0.106000 |
| C | 3.449000 | -2.393000 | -0.875000 |

| | | | |
|---|---|---|---|
| H | 4.345000 | -2.239000 | -1.152000 |
| C | 1.665000 | -3.877000 | -0.331000 |
| C | -3.081000 | -3.014000 | 1.027000 |
| H | -3.992000 | -3.038000 | 1.294000 |
| C | -1.525000 | -0.215000 | -4.055000 |
| H | -2.139000 | -0.745000 | -4.548000 |
| C | 2.996000 | -3.656000 | -0.726000 |
| H | 3.576000 | -4.392000 | -0.885000 |
| C | 1.100000 | 0.801000 | 4.674000 |
| H | 1.287000 | 0.972000 | 5.591000 |
| C | -2.795000 | 3.601000 | 1.716000 |
| H | -3.324000 | 4.306000 | 2.071000 |
| C | -0.621000 | 2.623000 | 4.589000 |
| H | -0.470000 | 2.855000 | 5.499000 |
| C | -2.399000 | -4.184000 | 0.859000 |
| H | -2.830000 | -5.018000 | 1.004000 |
| C | 1.653000 | 3.373000 | -3.702000 |
| H | 2.145000 | 4.088000 | -4.091000 |
| C | -1.543000 | 3.300000 | 3.874000 |
| H | -2.024000 | 4.005000 | 4.291000 |
| C | 0.812000 | 2.654000 | -4.467000 |
| H | 0.719000 | 2.877000 | -5.385000 |
| C | -0.843000 | 0.782000 | -4.680000 |
| H | -0.977000 | 0.947000 | -5.607000 |
| C | 2.659000 | 3.784000 | -1.429000 |
| H | 3.174000 | 4.517000 | -1.746000 |

| | | | |
|---|---|---|---|
| C | 1.071000 | -5.150000 | -0.128000 |
| H | 1.599000 | -5.928000 | -0.265000 |
| C | -0.218000 | -5.293000 | 0.253000 |
| H | -0.579000 | -6.164000 | 0.381000 |

**Figure S5. Experimental difference XANES (EXP) and fit result (FEFF) of HS state (FEFF calculation with ESCH optimization algorithm).**



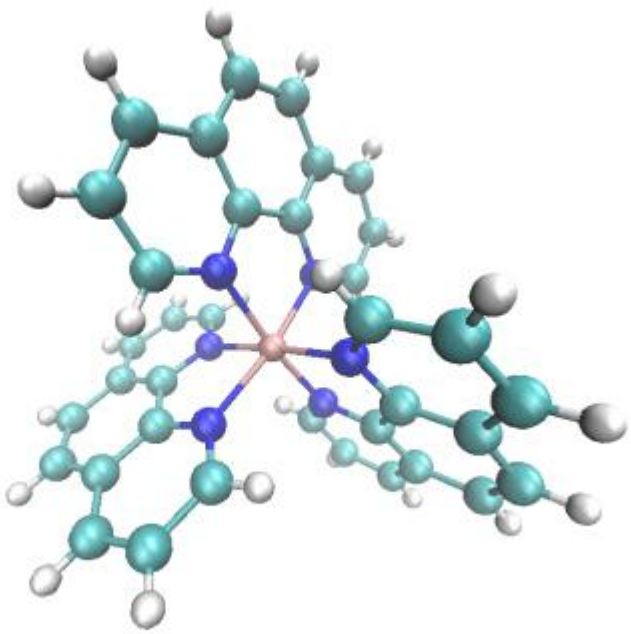



**Table S5. Fit result of HS state (FEFF with ESCH)**

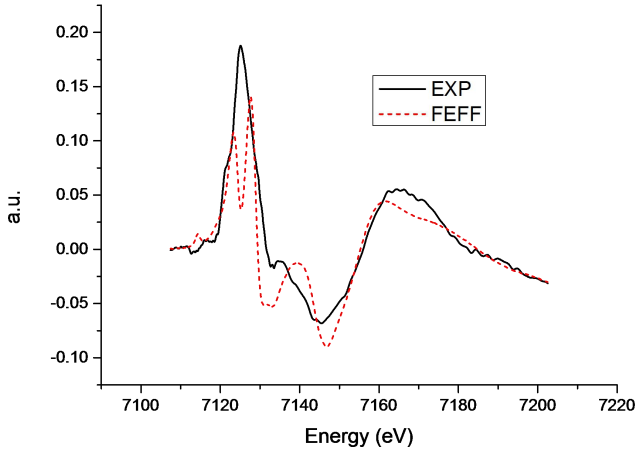
The coordinates of atoms in Fe(II)(phen)$_3$ complex for HS state with best fit in unit Å

| | | | |
|---|---|---|---|
| Fe | 0.000000 | 0.000000 | 0.000000 |
| N | 0.458000 | 0.113000 | 2.005000 |
| N | -1.131000 | -1.578000 | 0.238000 |
| N | 1.361000 | -1.348000 | -0.459000 |
| N | 1.186000 | 1.544000 | -0.460000 |
| N | -1.376000 | 1.372000 | 0.652000 |
| N | -0.462000 | 0.187000 | -1.953000 |
| C | -1.213000 | 1.774000 | 1.948000 |
| C | -0.228000 | 1.075000 | 2.690000 |
| C | -0.453000 | -2.757000 | 0.066000 |
| C | 1.360000 | -0.592000 | 2.681000 |
| H | 1.841000 | -1.272000 | 2.225000 |
| C | 0.917000 | -2.622000 | -0.326000 |
| C | 0.216000 | 1.186000 | -2.579000 |
| C | 1.108000 | 1.937000 | -1.765000 |
| C | -1.318000 | -0.539000 | -2.683000 |
| H | -1.804000 | -1.243000 | -2.267000 |
| C | -2.424000 | -1.663000 | 0.602000 |
| H | -2.925000 | -0.866000 | 0.717000 |
| C | -2.328000 | 1.968000 | -0.054000 |
| H | -2.480000 | 1.687000 | -0.949000 |
| C | 2.005000 | 2.247000 | 0.338000 |

| | | | |
|---|---|---|---|
| H | 2.088000 | 1.987000 | 1.247000 |
| C | 2.640000 | -1.194000 | -0.839000 |
| H | 2.981000 | -0.313000 | -0.939000 |
| C | -0.005000 | 1.379000 | 4.039000 |
| C | 2.745000 | 3.346000 | -0.116000 |
| H | 3.295000 | 3.831000 | 0.487000 |
| C | 0.074000 | 1.502000 | -3.935000 |
| C | 1.832000 | 3.011000 | -2.300000 |
| C | -1.012000 | -4.019000 | 0.253000 |
| C | -1.956000 | 2.804000 | 2.546000 |
| C | 1.633000 | -0.371000 | 4.042000 |
| H | 2.278000 | -0.902000 | 4.494000 |
| C | -3.123000 | 3.001000 | 0.473000 |
| H | -3.792000 | 3.407000 | -0.066000 |
| C | 3.485000 | -2.272000 | -1.088000 |
| H | 4.381000 | -2.118000 | -1.365000 |
| C | 1.701000 | -3.756000 | -0.544000 |
| C | -3.045000 | -2.893000 | 0.814000 |
| H | -3.956000 | -2.917000 | 1.081000 |
| C | -1.513000 | -0.284000 | -4.048000 |
| H | -2.127000 | -0.814000 | -4.541000 |
| C | 3.032000 | -3.535000 | -0.939000 |
| H | 3.612000 | -4.271000 | -1.098000 |
| C | 0.960000 | 0.621000 | 4.714000 |
| H | 1.147000 | 0.792000 | 5.631000 |
| C | -2.935000 | 3.421000 | 1.756000 |

| | | | |
|---|---|---|---|
| H | -3.464000 | 4.126000 | 2.111000 |
| C | -0.761000 | 2.443000 | 4.629000 |
| H | -0.610000 | 2.675000 | 5.539000 |
| C | -2.363000 | -4.063000 | 0.646000 |
| H | -2.794000 | -4.897000 | 0.791000 |
| C | 1.665000 | 3.304000 | -3.695000 |
| H | 2.157000 | 4.019000 | -4.084000 |
| C | -1.683000 | 3.120000 | 3.914000 |
| H | -2.164000 | 3.825000 | 4.331000 |
| C | 0.824000 | 2.585000 | -4.460000 |
| H | 0.731000 | 2.808000 | -5.378000 |
| C | -0.831000 | 0.713000 | -4.673000 |
| H | -0.965000 | 0.878000 | -5.600000 |
| C | 2.671000 | 3.715000 | -1.422000 |
| H | 3.186000 | 4.448000 | -1.739000 |
| C | 1.107000 | -5.029000 | -0.341000 |
| H | 1.635000 | -5.807000 | -0.478000 |
| C | -0.182000 | -5.172000 | 0.040000 |
| H | -0.543000 | -6.043000 | 0.168000 |

**Figure S6. Experimental difference XANES (EXP) and fit result (FEFF) of HS state (FEFF calculation with BOBYQA optimization algorithm).**



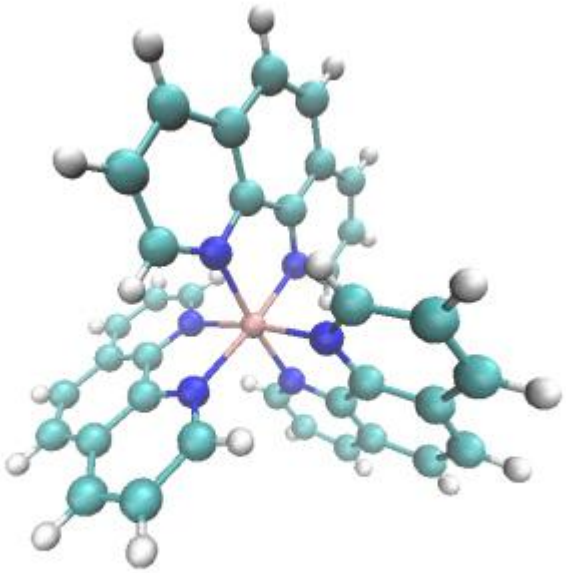



**Table S6. Fit result of HS state (FEFF with BOBYQA)**

The coordinates of atoms in Fe(II)(phen)$_3$ complex for HS state with best fit in unit Å

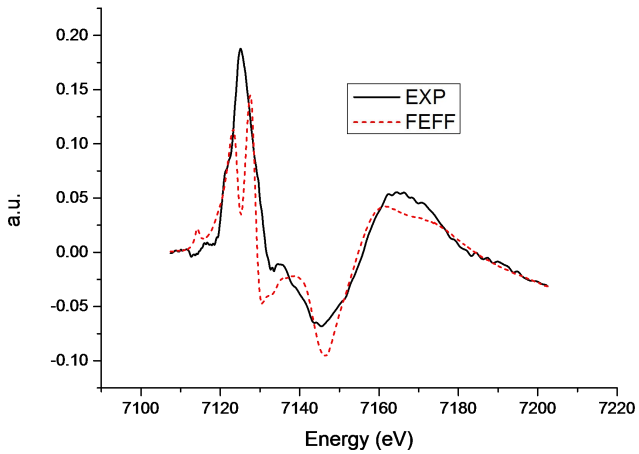
| | | | |
|---|---|---|---|
| Fe | 0.000000 | 0.000000 | 0.000000 |
| N | 0.473000 | 0.060000 | 1.925000 |
| N | -1.120000 | -1.713000 | 0.281000 |
| N | 1.372000 | -1.483000 | -0.416000 |

| | | | |
|---|---|---|---|
| N | 1.190000 | 1.513000 | -0.425000 |
| N | -1.361000 | 1.319000 | 0.572000 |
| N | -0.458000 | 0.156000 | -1.918000 |
| C | -1.198000 | 1.721000 | 1.868000 |
| C | -0.213000 | 1.022000 | 2.610000 |
| C | -0.442000 | -2.892000 | 0.109000 |
| C | 1.375000 | -0.645000 | 2.601000 |
| H | 1.856000 | -1.325000 | 2.145000 |
| C | 0.928000 | -2.757000 | -0.283000 |
| C | 0.220000 | 1.155000 | -2.544000 |
| C | 1.112000 | 1.906000 | -1.730000 |
| C | -1.314000 | -0.570000 | -2.648000 |
| H | -1.800000 | -1.274000 | -2.232000 |
| C | -2.413000 | -1.798000 | 0.645000 |
| H | -2.914000 | -1.001000 | 0.760000 |
| C | -2.313000 | 1.915000 | -0.134000 |
| H | -2.465000 | 1.634000 | -1.029000 |
| C | 2.009000 | 2.216000 | 0.373000 |
| H | 2.092000 | 1.956000 | 1.282000 |
| C | 2.651000 | -1.329000 | -0.796000 |
| H | 2.992000 | -0.448000 | -0.896000 |
| C | 0.010000 | 1.326000 | 3.959000 |
| C | 2.749000 | 3.315000 | -0.081000 |
| H | 3.299000 | 3.800000 | 0.522000 |
| C | 0.078000 | 1.471000 | -3.900000 |
| C | 1.836000 | 2.980000 | -2.265000 |

| | | | |
|---|---|---|---|
| C | -1.001000 | -4.154000 | 0.296000 |
| C | -1.941000 | 2.751000 | 2.466000 |
| C | 1.648000 | -0.424000 | 3.962000 |
| H | 2.293000 | -0.955000 | 4.414000 |
| C | -3.108000 | 2.948000 | 0.393000 |
| H | -3.777000 | 3.354000 | -0.146000 |
| C | 3.496000 | -2.407000 | -1.045000 |
| H | 4.392000 | -2.253000 | -1.322000 |
| C | 1.712000 | -3.891000 | -0.501000 |
| C | -3.034000 | -3.028000 | 0.857000 |
| H | -3.945000 | -3.052000 | 1.124000 |
| C | -1.509000 | -0.315000 | -4.013000 |
| H | -2.123000 | -0.845000 | -4.506000 |
| C | 3.043000 | -3.670000 | -0.896000 |
| H | 3.623000 | -4.406000 | -1.055000 |
| C | 0.975000 | 0.568000 | 4.634000 |
| H | 1.162000 | 0.739000 | 5.551000 |
| C | -2.920000 | 3.368000 | 1.676000 |
| H | -3.449000 | 4.073000 | 2.031000 |
| C | -0.746000 | 2.390000 | 4.549000 |
| H | -0.595000 | 2.622000 | 5.459000 |
| C | -2.352000 | -4.198000 | 0.689000 |
| H | -2.783000 | -5.032000 | 0.834000 |
| C | 1.669000 | 3.273000 | -3.660000 |
| H | 2.161000 | 3.988000 | -4.049000 |
| C | -1.668000 | 3.067000 | 3.834000 |

| | | | |
|---|---|---|---|
| H | -2.149000 | 3.772000 | 4.251000 |
| C | 0.828000 | 2.554000 | -4.425000 |
| H | 0.735000 | 2.777000 | -5.343000 |
| C | -0.827000 | 0.682000 | -4.638000 |
| H | -0.961000 | 0.847000 | -5.565000 |
| C | 2.675000 | 3.684000 | -1.387000 |
| H | 3.190000 | 4.417000 | -1.704000 |
| C | 1.118000 | -5.164000 | -0.298000 |
| H | 1.646000 | -5.942000 | -0.435000 |
| C | -0.171000 | -5.307000 | 0.083000 |
| H | -0.532000 | -6.178000 | 0.211000 |

**Figure S7. Experimental difference XANES (EXP) and fit result (FEFF) of HS state (FEFF calculation with COBYLA optimization algorithm).**



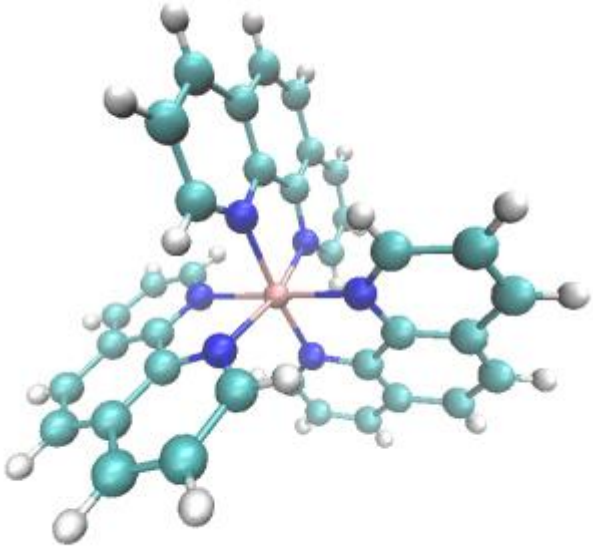


**Table S7. Fit result of HS state (FEFF with COBYLA)**

The coordinates of atoms in Fe(II)$(phen)_3$ complex for HS state with best fit in unit Å

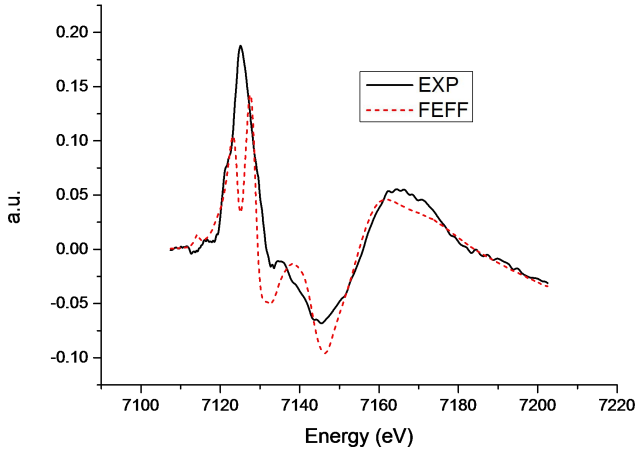
| | | | |
|---|---|---|---|
| Fe | 0.000000 | 0.000000 | 0.000000 |
| N | 0.474000 | 0.050000 | 1.913000 |
| N | -1.131000 | -1.693000 | 0.020000 |
| N | 1.361000 | -1.463000 | -0.677000 |
| N | 1.197000 | 1.510000 | -0.446000 |
| N | -1.360000 | 1.309000 | 0.560000 |
| N | -0.451000 | 0.153000 | -1.939000 |
| C | -1.197000 | 1.711000 | 1.856000 |
| C | -0.212000 | 1.012000 | 2.598000 |
| C | -0.453000 | -2.872000 | -0.152000 |
| C | 1.376000 | -0.655000 | 2.589000 |
| H | 1.857000 | -1.335000 | 2.133000 |

| | | | |
|---|---|---|---|
| C | 0.917000 | -2.737000 | -0.544000 |
| C | 0.227000 | 1.152000 | -2.565000 |
| C | 1.119000 | 1.903000 | -1.751000 |
| C | -1.307000 | -0.573000 | -2.669000 |
| H | -1.793000 | -1.277000 | -2.253000 |
| C | -2.424000 | -1.778000 | 0.384000 |
| H | -2.925000 | -0.981000 | 0.499000 |
| C | -2.312000 | 1.905000 | -0.146000 |
| H | -2.464000 | 1.624000 | -1.041000 |
| C | 2.016000 | 2.213000 | 0.352000 |
| H | 2.099000 | 1.953000 | 1.261000 |
| C | 2.640000 | -1.309000 | -1.057000 |
| H | 2.981000 | -0.428000 | -1.157000 |
| C | 0.011000 | 1.316000 | 3.947000 |
| C | 2.756000 | 3.312000 | -0.102000 |
| H | 3.306000 | 3.797000 | 0.501000 |
| C | 0.085000 | 1.468000 | -3.921000 |
| C | 1.843000 | 2.977000 | -2.286000 |
| C | -1.012000 | -4.134000 | 0.035000 |
| C | -1.940000 | 2.741000 | 2.454000 |
| C | 1.649000 | -0.434000 | 3.950000 |
| H | 2.294000 | -0.965000 | 4.402000 |
| C | -3.107000 | 2.938000 | 0.381000 |
| H | -3.776000 | 3.344000 | -0.158000 |
| C | 3.485000 | -2.387000 | -1.306000 |
| H | 4.381000 | -2.233000 | -1.583000 |

| | | | |
|---|---|---|---|
| C | 1.701000 | -3.871000 | -0.762000 |
| C | -3.045000 | -3.008000 | 0.596000 |
| H | -3.956000 | -3.032000 | 0.863000 |
| C | -1.502000 | -0.318000 | -4.034000 |
| H | -2.116000 | -0.848000 | -4.527000 |
| C | 3.032000 | -3.650000 | -1.157000 |
| H | 3.612000 | -4.386000 | -1.316000 |
| C | 0.976000 | 0.558000 | 4.622000 |
| H | 1.163000 | 0.729000 | 5.539000 |
| C | -2.919000 | 3.358000 | 1.664000 |
| H | -3.448000 | 4.063000 | 2.019000 |
| C | -0.745000 | 2.380000 | 4.537000 |
| H | -0.594000 | 2.612000 | 5.447000 |
| C | -2.363000 | -4.178000 | 0.428000 |
| H | -2.794000 | -5.012000 | 0.573000 |
| C | 1.676000 | 3.270000 | -3.681000 |
| H | 2.168000 | 3.985000 | -4.070000 |
| C | -1.667000 | 3.057000 | 3.822000 |
| H | -2.148000 | 3.762000 | 4.239000 |
| C | 0.835000 | 2.551000 | -4.446000 |
| H | 0.742000 | 2.774000 | -5.364000 |
| C | -0.820000 | 0.679000 | -4.659000 |
| H | -0.954000 | 0.844000 | -5.586000 |
| C | 2.682000 | 3.681000 | -1.408000 |
| H | 3.197000 | 4.414000 | -1.725000 |
| C | 1.107000 | -5.144000 | -0.559000 |

| | | | |
|---|---|---|---|
| H | 1.635000 | -5.922000 | -0.696000 |
| C | -0.182000 | -5.287000 | -0.178000 |
| H | -0.543000 | -6.158000 | -0.050000 |

**Figure S8. Experimental difference XANES (EXP) and fit result (FEFF) of HS state (FEFF calculation with SPBLX optimization algorithm).**



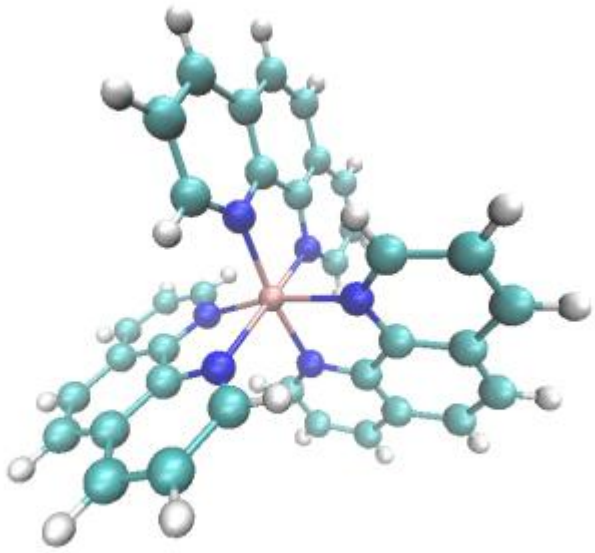



**Table S8. Fit result of HS state (FEFF with SPBLX)**

The coordinates of atoms in Fe(II)$(phen)_3$ complex for HS state with best fit in unit Å

| | | | |
|---|---|---|---|
| Fe | 0.000000 | 0.000000 | 0.000000 |
| N | 0.490000 | 0.123000 | 1.995000 |
| N | -1.100000 | -1.725000 | 0.515000 |
| N | 1.392000 | -1.495000 | -0.182000 |
| N | 1.171000 | 1.528000 | -0.433000 |
| N | -1.344000 | 1.382000 | 0.642000 |
| N | -0.477000 | 0.171000 | -1.926000 |
| C | -1.181000 | 1.784000 | 1.938000 |
| C | -0.196000 | 1.085000 | 2.680000 |
| C | -0.422000 | -2.904000 | 0.343000 |
| C | 1.392000 | -0.582000 | 2.671000 |
| H | 1.873000 | -1.262000 | 2.215000 |
| C | 0.948000 | -2.769000 | -0.049000 |
| C | 0.201000 | 1.170000 | -2.552000 |
| C | 1.093000 | 1.921000 | -1.738000 |
| C | -1.333000 | -0.555000 | -2.656000 |
| H | -1.819000 | -1.259000 | -2.240000 |
| C | -2.393000 | -1.810000 | 0.879000 |
| H | -2.894000 | -1.013000 | 0.994000 |
| C | -2.296000 | 1.978000 | -0.064000 |
| H | -2.448000 | 1.697000 | -0.959000 |
| C | 1.990000 | 2.231000 | 0.365000 |
| H | 2.073000 | 1.971000 | 1.274000 |

| | | | |
|---|---|---|---|
| C | 2.671000 | -1.341000 | -0.562000 |
| H | 3.012000 | -0.460000 | -0.662000 |
| C | 0.027000 | 1.389000 | 4.029000 |
| C | 2.730000 | 3.330000 | -0.089000 |
| H | 3.280000 | 3.815000 | 0.514000 |
| C | 0.059000 | 1.486000 | -3.908000 |
| C | 1.817000 | 2.995000 | -2.273000 |
| C | -0.981000 | -4.166000 | 0.530000 |
| C | -1.924000 | 2.814000 | 2.536000 |
| C | 1.665000 | -0.361000 | 4.032000 |
| H | 2.310000 | -0.892000 | 4.484000 |
| C | -3.091000 | 3.011000 | 0.463000 |
| H | -3.760000 | 3.417000 | -0.076000 |
| C | 3.516000 | -2.419000 | -0.811000 |
| H | 4.412000 | -2.265000 | -1.088000 |
| C | 1.732000 | -3.903000 | -0.267000 |
| C | -3.014000 | -3.040000 | 1.091000 |
| H | -3.925000 | -3.064000 | 1.358000 |
| C | -1.528000 | -0.300000 | -4.021000 |
| H | -2.142000 | -0.830000 | -4.514000 |
| C | 3.063000 | -3.682000 | -0.662000 |
| H | 3.643000 | -4.418000 | -0.821000 |
| C | 0.992000 | 0.631000 | 4.704000 |
| H | 1.179000 | 0.802000 | 5.621000 |
| C | -2.903000 | 3.431000 | 1.746000 |
| H | -3.432000 | 4.136000 | 2.101000 |

| | | | |
|---|---|---|---|
| C | -0.729000 | 2.453000 | 4.619000 |
| H | -0.578000 | 2.685000 | 5.529000 |
| C | -2.332000 | -4.210000 | 0.923000 |
| H | -2.763000 | -5.044000 | 1.068000 |
| C | 1.650000 | 3.288000 | -3.668000 |
| H | 2.142000 | 4.003000 | -4.057000 |
| C | -1.651000 | 3.130000 | 3.904000 |
| H | -2.132000 | 3.835000 | 4.321000 |
| C | 0.809000 | 2.569000 | -4.433000 |
| H | 0.716000 | 2.792000 | -5.351000 |
| C | -0.846000 | 0.697000 | -4.646000 |
| H | -0.980000 | 0.862000 | -5.573000 |
| C | 2.656000 | 3.699000 | -1.395000 |
| H | 3.171000 | 4.432000 | -1.712000 |
| C | 1.138000 | -5.176000 | -0.064000 |
| H | 1.666000 | -5.954000 | -0.201000 |
| C | -0.151000 | -5.319000 | 0.317000 |
| H | -0.512000 | -6.190000 | 0.445000 |

**Table S9. Fit result of HS state (FEFF with NOMAD)**

The coordinates of atoms in Fe(II)(phen)$_3$ complex for HS state with best fit in unit Å

| | | | |
|---|---|---|---|
| Fe | 0.00000000 | 0.00000000 | 0.00000000 |
| N | 0.36600000 | 0.04300000 | 2.00400000 |
| N | -1.22200000 | -1.67000000 | -0.18700000 |
| N | 1.27000000 | -1.44000000 | -0.88400000 |

| | | | |
|---|---|---|---|
| N | 1.13200000 | 1.63700000 | -0.54900000 |
| N | -1.46800000 | 1.30200000 | 0.65100000 |
| N | -0.51600000 | 0.28000000 | -2.04200000 |
| C | -1.30500000 | 1.70400000 | 1.94700000 |
| C | -0.32000000 | 1.00500000 | 2.68900000 |
| C | -0.54400000 | -2.84900000 | -0.35900000 |
| C | 1.26800000 | -0.66200000 | 2.68000000 |
| H | 1.74900000 | -1.34200000 | 2.22400000 |
| C | 0.82600000 | -2.71400000 | -0.75100000 |
| C | 0.16200000 | 1.27900000 | -2.66800000 |
| C | 1.05400000 | 2.03000000 | -1.85400000 |
| C | -1.37200000 | -0.44600000 | -2.77200000 |
| H | -1.85800000 | -1.15000000 | -2.35600000 |
| C | -2.51500000 | -1.75500000 | 0.17700000 |
| H | -3.01600000 | -0.95800000 | 0.29200000 |
| C | -2.42000000 | 1.89800000 | -0.05500000 |
| H | -2.57200000 | 1.61700000 | -0.95000000 |
| C | 1.95100000 | 2.34000000 | 0.24900000 |
| H | 2.03400000 | 2.08000000 | 1.15800000 |
| C | 2.54900000 | -1.28600000 | -1.26400000 |
| H | 2.89000000 | -0.40500000 | -1.36400000 |

| | | | |
|---|---|---|---|
| C | -0.09700000 | 1.30900000 | 4.03800000 |
| C | 2.69100000 | 3.43900000 | -0.20500000 |
| H | 3.24100000 | 3.92400000 | 0.39800000 |
| C | 0.02000000 | 1.59500000 | -4.02400000 |
| C | 1.77800000 | 3.10400000 | -2.38900000 |
| C | -1.10300000 | -4.11100000 | -0.17200000 |
| C | -2.04800000 | 2.73400000 | 2.54500000 |
| C | 1.54100000 | -0.44100000 | 4.04100000 |
| H | 2.18600000 | -0.97200000 | 4.49300000 |
| C | -3.21500000 | 2.93100000 | 0.47200000 |
| H | -3.88400000 | 3.33700000 | -0.06700000 |
| C | 3.39400000 | -2.36400000 | -1.51300000 |
| H | 4.29000000 | -2.21000000 | -1.79000000 |
| C | 1.61000000 | -3.84800000 | -0.96900000 |
| C | -3.13600000 | -2.98500000 | 0.38900000 |
| H | -4.04700000 | -3.00900000 | 0.65600000 |
| C | -1.56700000 | -0.19100000 | -4.13700000 |
| H | -2.18100000 | -0.72100000 | -4.63000000 |
| C | 2.94100000 | -3.62700000 | -1.36400000 |
| H | 3.52100000 | -4.36300000 | -1.52300000 |
| C | 0.86800000 | 0.55100000 | 4.71300000 |

| | | | |
|---|---|---|---|
| H | 1.05500000 | 0.72200000 | 5.63000000 |
| C | -3.02700000 | 3.35100000 | 1.75500000 |
| H | -3.55600000 | 4.05600000 | 2.11000000 |
| C | -0.85300000 | 2.37300000 | 4.62800000 |
| H | -0.70200000 | 2.60500000 | 5.53800000 |
| C | -2.45400000 | -4.15500000 | 0.22100000 |
| H | -2.88500000 | -4.98900000 | 0.36600000 |
| C | 1.61100000 | 3.39700000 | -3.78400000 |
| H | 2.10300000 | 4.11200000 | -4.17300000 |
| C | -1.77500000 | 3.05000000 | 3.91300000 |
| H | -2.25600000 | 3.75500000 | 4.33000000 |
| C | 0.77000000 | 2.67800000 | -4.54900000 |
| H | 0.67700000 | 2.90100000 | -5.46700000 |
| C | -0.88500000 | 0.80600000 | -4.76200000 |
| H | -1.01900000 | 0.97100000 | -5.68900000 |
| C | 2.61700000 | 3.80800000 | -1.51100000 |
| H | 3.13200000 | 4.54100000 | -1.82800000 |
| C | 1.01600000 | -5.12100000 | -0.76600000 |
| H | 1.54400000 | -5.89900000 | -0.90300000 |
| C | -0.27300000 | -5.26400000 | -0.38500000 |
| H | -0.63400000 | -6.13500000 | -0.25700000 |

**Table S10. Fit result of HS state (FDMNES calculation with NOMAD optimization algorithm)**

The coordinates of atoms in Fe(II)(phen)$_3$ complex for HS state with best fit in unit Å

| | | | |
|---|---|---|---|
| Fe | 0.00000000 | 0.00000000 | 0.00000000 |
| N | 0.41700000 | 0.14500000 | 2.07900000 |
| N | -1.11500000 | -1.77900000 | 0.40500000 |
| N | 1.37700000 | -1.54900000 | -0.29200000 |
| N | 1.19000000 | 1.51300000 | -0.42500000 |
| N | -1.41700000 | 1.40400000 | 0.72600000 |
| N | -0.45800000 | 0.15600000 | -1.91800000 |
| C | -1.25400000 | 1.80600000 | 2.02200000 |
| C | -0.26900000 | 1.10700000 | 2.76400000 |
| C | -0.43700000 | -2.95800000 | 0.23300000 |
| C | 1.31900000 | -0.56000000 | 2.75500000 |
| H | 1.80000000 | -1.24000000 | 2.29900000 |
| C | 0.93300000 | -2.82300000 | -0.15900000 |
| C | 0.22000000 | 1.15500000 | -2.54400000 |
| C | 1.11200000 | 1.90600000 | -1.73000000 |
| C | -1.31400000 | -0.57000000 | -2.64800000 |
| H | -1.80000000 | -1.27400000 | -2.23200000 |
| C | -2.40800000 | -1.86400000 | 0.76900000 |

| | | | |
|---|---|---|---|
| H | -2.90900000 | -1.06700000 | 0.88400000 |
| C | -2.36900000 | 2.00000000 | 0.02000000 |
| H | -2.52100000 | 1.71900000 | -0.87500000 |
| C | 2.00900000 | 2.21600000 | 0.37300000 |
| H | 2.09200000 | 1.95600000 | 1.28200000 |
| C | 2.65600000 | -1.39500000 | -0.67200000 |
| H | 2.99700000 | -0.51400000 | -0.77200000 |
| C | -0.04600000 | 1.41100000 | 4.11300000 |
| C | 2.74900000 | 3.31500000 | -0.08100000 |
| H | 3.29900000 | 3.80000000 | 0.52200000 |
| C | 0.07800000 | 1.47100000 | -3.90000000 |
| C | 1.83600000 | 2.98000000 | -2.26500000 |
| C | -0.99600000 | -4.22000000 | 0.42000000 |
| C | -1.99700000 | 2.83600000 | 2.62000000 |
| C | 1.59200000 | -0.33900000 | 4.11600000 |
| H | 2.23700000 | -0.87000000 | 4.56800000 |
| C | -3.16400000 | 3.03300000 | 0.54700000 |
| H | -3.83300000 | 3.43900000 | 0.00800000 |
| C | 3.50100000 | -2.47300000 | -0.92100000 |
| H | 4.39700000 | -2.31900000 | -1.19800000 |
| C | 1.71700000 | -3.95700000 | -0.37700000 |

| | | | |
|---|---|---|---|
| C | -3.02900000 | -3.09400000 | 0.98100000 |
| H | -3.94000000 | -3.11800000 | 1.24800000 |
| C | -1.50900000 | -0.31500000 | -4.01300000 |
| H | -2.12300000 | -0.84500000 | -4.50600000 |
| C | 3.04800000 | -3.73600000 | -0.77200000 |
| H | 3.62800000 | -4.47200000 | -0.93100000 |
| C | 0.91900000 | 0.65300000 | 4.78800000 |
| H | 1.10600000 | 0.82400000 | 5.70500000 |
| C | -2.97600000 | 3.45300000 | 1.83000000 |
| H | -3.50500000 | 4.15800000 | 2.18500000 |
| C | -0.80200000 | 2.47500000 | 4.70300000 |
| H | -0.65100000 | 2.70700000 | 5.61300000 |
| C | -2.34700000 | -4.26400000 | 0.81300000 |
| H | -2.77800000 | -5.09800000 | 0.95800000 |
| C | 1.66900000 | 3.27300000 | -3.66000000 |
| H | 2.16100000 | 3.98800000 | -4.04900000 |
| C | -1.72400000 | 3.15200000 | 3.98800000 |
| H | -2.20500000 | 3.85700000 | 4.40500000 |
| C | 0.82800000 | 2.55400000 | -4.42500000 |
| H | 0.73500000 | 2.77700000 | -5.34300000 |
| C | -0.82700000 | 0.68200000 | -4.63800000 |

| | | | |
|---|---|---|---|
| H | -0.96100000 | 0.84700000 | -5.56500000 |
| C | 2.67500000 | 3.68400000 | -1.38700000 |
| H | 3.19000000 | 4.41700000 | -1.70400000 |
| C | 1.12300000 | -5.23000000 | -0.17400000 |
| H | 1.65100000 | -6.00800000 | -0.31100000 |
| C | -0.16600000 | -5.37300000 | 0.20700000 |
| H | -0.52700000 | -6.24400000 | 0.33500000 |