Electronic Supporting Information for:

Spectroscopic and Computational Studies of Reversible O_2 Binding by a Cobalt Complex of Relevance to Cysteine Dioxygenase

Anne A. Fischer, Sergey V. Lindeman, and Adam T. Fiedler*

Department of Chemistry, Marquette University, Milwaukee, WI 53201-1881

Email: adam.fiedler@marquette.edu

Contents

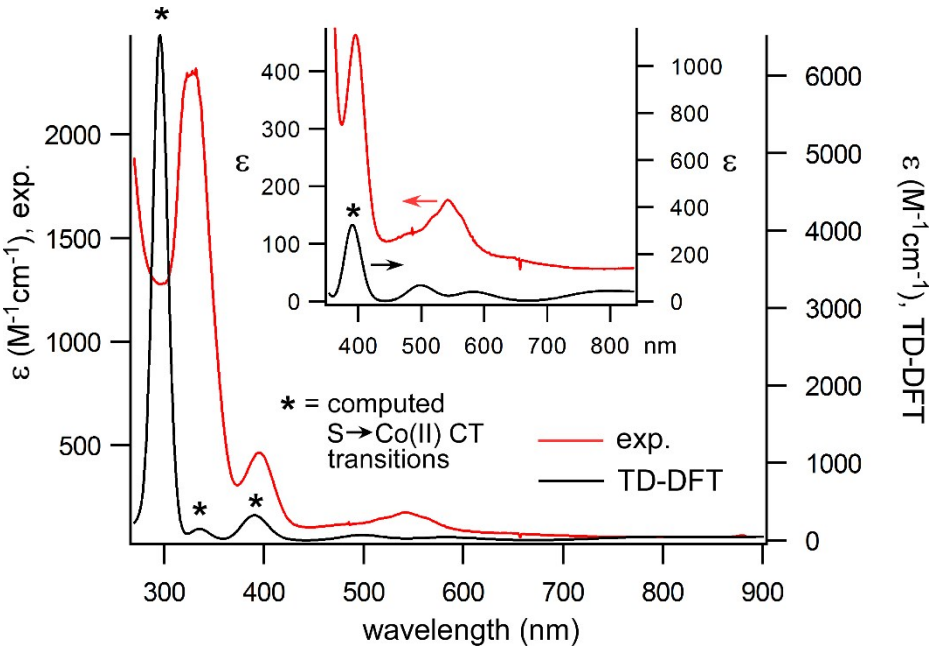

Figure S1. Comparison of TD-DFT computed (black line) and experimental (red line) absorption spectra obtained for a truncated [Co(Tp^{R2})(CysOEt)] model. Features in the computed spectrum arising from S→Co(II) CT transitions are indicated with an asterisk. *Inset:* Enlargement of computed and experimental features in the visible region.

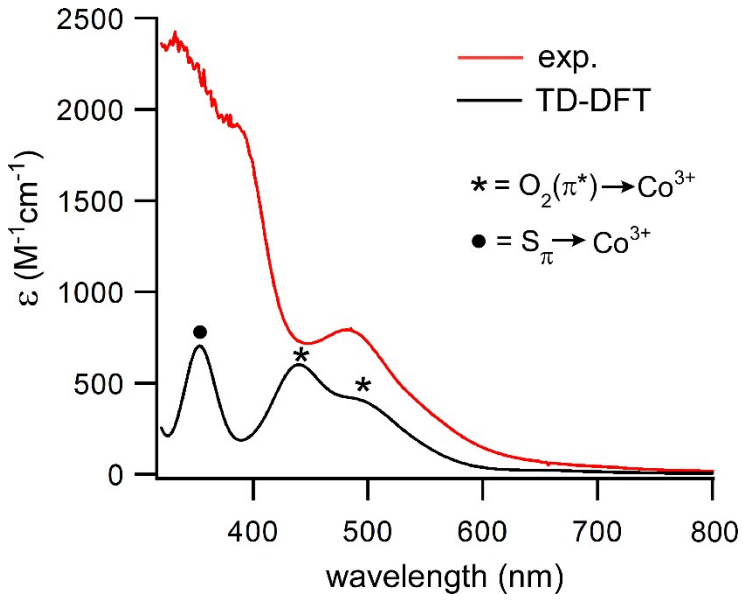

Figure S2. Comparison of TD-DFT computed (black line) and experimental (red line) absorption spectra obtained for **4-O$_2$**. The dominant transition for each computed absorption feature is indicated by the * and ● symbols.

Table S1. Thermodynamic Parameters Computed by DFT for the Reaction of Fe- and Co-CDO Models with O_2 to Yield the *S*-Dioxygenated Product.[a]

Intermediate [b]	Metal Ion	Spin-State	ΔH (or $\Delta H^{\ddagger}$)	$-T\Delta S$ (or $-T\Delta S^{\ddagger}$)	ΔG (or $\Delta G^{\ddagger}$)
A	Fe	$S = 2$	-0.3	11.2	10.9
	Co	$S = 1/2$	-10.4	15.9	5.5
	Co	$S = 3/2$	2.9	13.2	16.2
TS1	Fe	$S = 2$	10.2	14.9	25.1
	Co	$S = 1/2$	17.3	19.0	36.3
	Co	$S = 3/2$	13.0	15.9	28.9
B	Fe	$S = 2$	-0.3	12.5	12.2
	Co	$S = 1/2$	2.4	14.6	17.1
	Co	$S = 3/2$	-0.4	13.7	13.3
TS2	Fe	$S = 2$	0.8	15.2	16.0
	Co	$S = 1/2$	6.9	18.7	25.6
	Co	$S = 3/2$	4.0	15.9	19.9
C	Fe	$S = 2$	-20.3	12.2	-8.1
	Co	$S = 1/2$	-10.9	15.5	4.5
	Co	$S = 3/2$	-13.2	12.6	-0.5
TS3	Fe	$S = 2$	-13.3	15.0	1.8
	Co	$S = 1/2$	-2.8	18.6	15.8
	Co	$S = 3/2$	-8.8	17.3	8.5
D	Fe	$S = 2$	-48.5	12.5	-36.1
	Co	$S = 1/2$	-44.2	14.7	-29.5
	Co	$S = 3/2$	-45.4	13.0	-32.4

[a] All energies (reported in kcal/mol) are relative to M(II) precursors and O_2.

[b] The identities of reaction intermediates and transition states are provided in the main text (see Scheme 2 and Figure 10).

Table 2. Cartesian Coordinates (Å) of the DFT-Optimized Co(II) Complex ($S = 3/2$).

Co	0.026665000000	0.098235000000	0.014985000000
S	2.275000000000	0.416635000000	0.087647000000
H	2.731818000000	1.079090000000	-2.213743000000
C	2.733490000000	0.122368000000	-1.670348000000
N	0.395726000000	-0.437446000000	-2.124918000000
N	-0.570935000000	0.452008000000	2.036516000000
H	3.757347000000	-0.267851000000	-1.714905000000
C	1.790701000000	-0.858773000000	-2.340427000000
N	-1.917492000000	0.512804000000	2.231339000000
C	-2.185444000000	0.759112000000	3.529820000000
H	2.032863000000	-0.957228000000	-3.412799000000
C	-0.982761000000	0.867517000000	4.205621000000
N	-2.695148000000	-1.065187000000	0.444309000000
H	1.912000000000	-1.845407000000	-1.877863000000
C	0.009284000000	0.671321000000	3.228289000000
H	-0.833515000000	1.068090000000	5.259239000000
N	-1.466039000000	-1.461031000000	0.030781000000
H	1.748656000000	0.974960000000	4.424564000000
C	1.488883000000	0.702272000000	3.396372000000
N	-2.599267000000	1.439919000000	-0.001846000000
H	1.951309000000	1.429515000000	2.719274000000
N	-1.350508000000	1.561765000000	-0.517982000000
H	1.942870000000	-0.269844000000	3.168861000000
H	-3.208720000000	0.842683000000	3.875817000000
C	-1.546072000000	-2.768633000000	-0.262716000000
C	-2.859510000000	-3.220660000000	-0.039275000000
H	-3.243598000000	-4.223903000000	-0.176208000000
C	-3.549125000000	-2.109596000000	0.413395000000
H	-4.577321000000	-1.988598000000	0.731633000000
H	0.068189000000	4.241691000000	-1.760656000000
H	-0.059922000000	2.963164000000	-2.970499000000
H	0.808246000000	2.663640000000	-1.438737000000
C	-0.354242000000	-3.542240000000	-0.718866000000
H	-0.385194000000	-4.564879000000	-0.327028000000
H	0.570158000000	-3.073633000000	-0.363073000000
H	-0.298815000000	-3.621038000000	-1.814423000000
H	-4.384584000000	2.574661000000	-0.064813000000
C	-1.315890000000	2.699646000000	-1.230585000000
H	-2.877018000000	4.244641000000	-1.653375000000
C	-2.578514000000	3.315523000000	-1.183985000000
C	-3.355435000000	2.486510000000	-0.391189000000
C	-0.059279000000	3.160619000000	-1.888601000000
B	-2.902638000000	0.343570000000	1.052574000000
H	-4.040131000000	0.456877000000	1.439138000000
H	0.190765000000	0.403402000000	-2.666226000000
H	-0.263089000000	-1.150536000000	-2.435763000000

Table 3. Cartesian Coordinates (Å) of the DFT-Optimized Co(II) Complex ($S = 1/2$).

Co	-0.033815000000	-0.000501000000	0.045705000000
S	2.013576000000	0.899161000000	0.158979000000
H	2.425471000000	1.398318000000	-2.211216000000
C	2.605036000000	0.540691000000	-1.546027000000
N	0.434903000000	-0.489715000000	-1.819404000000
N	-0.528894000000	0.385139000000	1.915910000000
H	3.687280000000	0.367546000000	-1.524422000000
C	1.884735000000	-0.679310000000	-2.068417000000
N	-1.854182000000	0.614518000000	2.145598000000
C	-2.065208000000	0.804318000000	3.463092000000
H	2.080749000000	-0.855309000000	-3.139833000000
C	-0.853092000000	0.696327000000	4.116130000000
N	-2.732830000000	-0.968010000000	0.451861000000
H	2.201814000000	-1.565489000000	-1.506704000000
C	0.092422000000	0.424614000000	3.111172000000
H	-0.662270000000	0.793459000000	5.177434000000
N	-1.499411000000	-1.363624000000	0.056266000000
H	1.743350000000	-0.137924000000	4.326099000000
C	1.552023000000	0.195666000000	3.299681000000
N	-2.633763000000	1.499544000000	-0.075227000000
H	2.131643000000	1.110274000000	3.124402000000
N	-1.406069000000	1.531906000000	-0.646270000000
H	1.936310000000	-0.554887000000	2.603798000000
H	-3.064701000000	0.992311000000	3.835406000000
C	-1.565343000000	-2.683346000000	-0.202425000000
C	-2.877511000000	-3.135045000000	0.023439000000
H	-3.252403000000	-4.144820000000	-0.087636000000
C	-3.577996000000	-2.017863000000	0.445034000000
H	-4.608589000000	-1.895919000000	0.754653000000
H	-0.182782000000	4.082574000000	-2.449132000000
H	-0.018621000000	2.460003000000	-3.108930000000
H	0.751828000000	2.862549000000	-1.553057000000
C	-0.364723000000	-3.472506000000	-0.606477000000
H	-0.390620000000	-4.469347000000	-0.152578000000
H	0.553354000000	-2.976423000000	-0.271433000000
H	-0.300124000000	-3.623559000000	-1.694384000000
H	-4.373992000000	2.709554000000	-0.098317000000
C	-1.365110000000	2.632197000000	-1.416506000000
H	-2.874771000000	4.225923000000	-1.848880000000
C	-2.596802000000	3.309457000000	-1.342966000000
C	-3.368712000000	2.559579000000	-0.473265000000
C	-0.138745000000	3.024087000000	-2.171493000000
B	-2.908335000000	0.460953000000	1.022914000000
H	-4.019910000000	0.598993000000	1.471843000000
H	0.093148000000	0.289305000000	-2.386531000000
H	-0.094558000000	-1.309613000000	-2.118558000000

Table 4. Cartesian Coordinates (Å) of the DFT-Optimized $\mathbf{A}^{\mathbf{Co},S=1/2}$ Model.

Co	-0.006263000000	-0.126389000000	-0.101623000000
O	-0.242715000000	-0.235237000000	1.789859000000
O	0.781462000000	-0.313641000000	2.580801000000
S	0.002704000000	2.136395000000	0.019660000000
C	1.543647000000	2.241651000000	1.002578000000
C	2.564712000000	1.303003000000	0.396392000000
N	1.946817000000	-0.039407000000	0.192629000000
H	2.000730000000	-0.526955000000	1.096049000000
H	2.461305000000	-0.577190000000	-0.505146000000
N	-0.799837000000	-2.746813000000	-1.123392000000
C	-0.727966000000	-4.089081000000	-1.093229000000
B	-1.678634000000	-1.844204000000	-2.010535000000
N	0.057750000000	-2.202481000000	-0.223598000000
H	-1.253798000000	-1.415837000000	-4.802681000000
H	-1.350121000000	-4.685883000000	-1.748660000000
H	-4.517578000000	-1.550490000000	-1.644931000000
C	0.209285000000	-4.444709000000	-0.141109000000
N	-2.558955000000	-0.983276000000	-1.100158000000
C	0.682836000000	-3.233617000000	0.387961000000
N	-1.989810000000	-0.194218000000	-0.152553000000
C	-3.898602000000	-0.972021000000	-0.970219000000
N	-0.749322000000	-0.927624000000	-2.812913000000
C	-4.216402000000	-0.151316000000	0.093670000000
N	0.107678000000	-0.081877000000	-2.181272000000
C	-2.990262000000	0.316711000000	0.598573000000
C	-0.635024000000	-0.814910000000	-4.147746000000
C	0.331331000000	0.135676000000	-4.411755000000
C	0.776363000000	0.576585000000	-3.155426000000
C	1.720517000000	-3.099235000000	1.450750000000
C	-2.815773000000	1.182574000000	1.797544000000
C	1.826895000000	1.606459000000	-2.934683000000
H	-2.354881000000	-2.514325000000	-2.749698000000
H	0.518756000000	-5.440992000000	0.148864000000
H	-5.200020000000	0.090535000000	0.475900000000
H	0.679266000000	0.483338000000	-5.376358000000
H	1.939344000000	-4.086239000000	1.870719000000
H	2.668494000000	-2.707766000000	1.055226000000
H	1.396305000000	-2.448078000000	2.268431000000
H	-3.749753000000	1.717434000000	2.002790000000
H	-2.008036000000	1.904965000000	1.654177000000
H	-2.564657000000	0.575619000000	2.675764000000
H	2.012882000000	2.147846000000	-3.868290000000
H	1.511428000000	2.318037000000	-2.165245000000
H	2.782059000000	1.154617000000	-2.631491000000
H	3.452794000000	1.198188000000	1.038718000000
H	2.892057000000	1.683565000000	-0.571533000000
H	1.353366000000	1.984792000000	2.050773000000
H	1.909380000000	3.275666000000	0.967881000000

Table 5. Cartesian Coordinates (Å) of the DFT-Optimized $\mathbf{A}^{Co,S=3/2}$ Model.

Co	0.071885000000	-0.115050000000	-0.110488000000
O	-0.137833000000	-0.256395000000	1.844503000000
O	0.850696000000	-0.224676000000	2.660791000000
S	0.125014000000	2.109044000000	0.078515000000
C	1.630716000000	2.242962000000	1.102003000000
C	2.751571000000	1.402099000000	0.505400000000
N	2.290128000000	0.017998000000	0.279928000000
H	2.353200000000	-0.495082000000	1.159721000000
H	2.873195000000	-0.456378000000	-0.407529000000
N	-0.829456000000	-2.746081000000	-1.129506000000
C	-0.785570000000	-4.088244000000	-1.082352000000
B	-1.744628000000	-1.852039000000	-2.000471000000
N	0.067230000000	-2.214632000000	-0.256907000000
H	-1.414296000000	-1.351182000000	-4.792780000000
H	-1.438193000000	-4.679582000000	-1.712790000000
H	-4.612678000000	-1.620567000000	-1.689454000000
C	0.169214000000	-4.457689000000	-0.149785000000
N	-2.667225000000	-1.036624000000	-1.091255000000
C	0.683938000000	-3.253098000000	0.349031000000
N	-2.128274000000	-0.231939000000	-0.143264000000
C	-4.013558000000	-1.028344000000	-1.008225000000
N	-0.835264000000	-0.909302000000	-2.811930000000
C	-4.368143000000	-0.185964000000	0.029890000000
N	0.077499000000	-0.106706000000	-2.204928000000
C	-3.152372000000	0.291653000000	0.554388000000
C	-0.757664000000	-0.779395000000	-4.148679000000
C	0.236283000000	0.139006000000	-4.434397000000
C	0.741616000000	0.537663000000	-3.187459000000
C	1.758106000000	-3.106224000000	1.371538000000
C	-2.961454000000	1.202988000000	1.717692000000
C	1.849592000000	1.501939000000	-2.951287000000
H	-2.391419000000	-2.541689000000	-2.749741000000
H	0.463040000000	-5.458923000000	0.139610000000
H	-5.365425000000	0.056514000000	0.375815000000
H	0.565215000000	0.482753000000	-5.407116000000
H	1.965540000000	-4.077865000000	1.831202000000
H	2.698960000000	-2.758170000000	0.922867000000
H	1.477713000000	-2.410426000000	2.168864000000
H	-3.923345000000	1.620360000000	2.034116000000
H	-2.282157000000	2.026302000000	1.471923000000
H	-2.520043000000	0.665742000000	2.565848000000
H	2.126802000000	1.991416000000	-3.890710000000
H	1.555329000000	2.268251000000	-2.226308000000
H	2.746792000000	0.997315000000	-2.567127000000
H	3.631873000000	1.430576000000	1.167619000000
H	3.051478000000	1.826297000000	-0.457278000000
H	1.410042000000	1.913377000000	2.125544000000
H	1.928082000000	3.297863000000	1.146425000000

Table 6. Cartesian Coordinates (Å) for **TS1** (Co; $S = 1/2$).

Co	0.068058000000	-0.292954000000	-0.022616000000
O	-0.141501000000	-0.415822000000	1.831540000000
O	0.428966000000	0.754129000000	2.254633000000
S	0.243604000000	1.903428000000	0.536362000000
C	2.052927000000	2.095536000000	0.694629000000
C	2.790581000000	0.928435000000	0.047806000000
N	2.066271000000	-0.323876000000	0.315599000000
H	2.066443000000	-0.517503000000	1.326484000000
H	2.496572000000	-1.115779000000	-0.175819000000
N	-0.678187000000	-2.847521000000	-1.151238000000
C	-0.638125000000	-4.192978000000	-1.068604000000
B	-1.504238000000	-1.924186000000	-2.063571000000
N	0.064082000000	-2.291883000000	-0.173624000000
H	-1.028253000000	-1.392515000000	-4.825368000000
H	-1.192853000000	-4.808193000000	-1.782116000000
H	-4.374525000000	-1.599218000000	-1.870806000000
C	0.166361000000	-4.529951000000	0.014629000000
N	-2.435619000000	-1.078591000000	-1.172778000000
C	0.583760000000	-3.298676000000	0.564684000000
N	-1.923317000000	-0.311894000000	-0.180058000000
C	-3.786773000000	-1.036054000000	-1.140602000000
N	-0.552342000000	-0.965437000000	-2.800581000000
C	-4.165286000000	-0.214776000000	-0.088179000000
N	0.133769000000	-0.016593000000	-2.115640000000
C	-2.955022000000	0.216085000000	0.506748000000
C	-0.507477000000	-0.729823000000	-4.128845000000
C	0.232016000000	0.424394000000	-4.332105000000
C	0.601134000000	0.858326000000	-3.039477000000
C	1.425737000000	-3.097676000000	1.785476000000
C	-2.823507000000	1.073035000000	1.724443000000
C	1.306612000000	2.145631000000	-2.751461000000
H	-2.150122000000	-2.583268000000	-2.866792000000
H	0.416709000000	-5.528472000000	0.382047000000
H	-5.178098000000	0.046370000000	0.229107000000
H	0.463105000000	0.920453000000	-5.278345000000
H	1.412234000000	-4.017023000000	2.401598000000
H	2.490216000000	-2.893696000000	1.538675000000
H	1.030649000000	-2.253971000000	2.384936000000
H	-3.392018000000	2.016449000000	1.599198000000
H	-1.774692000000	1.311919000000	1.969036000000
H	-3.250480000000	0.542504000000	2.600192000000
H	1.026594000000	2.890911000000	-3.521405000000
H	0.999957000000	2.537670000000	-1.761663000000
H	2.412689000000	2.053342000000	-2.782116000000
H	3.837668000000	0.875064000000	0.420419000000
H	2.832839000000	1.054012000000	-1.046875000000
H	2.274026000000	2.155487000000	1.778314000000
H	2.350611000000	3.054996000000	0.225596000000

Table 7. Cartesian Coordinates (Å) for **TS1** (Co; $S = 3/2$).

Co	0.041484000000	-0.194260000000	0.034245000000
O	-0.027982000000	-0.228649000000	2.022245000000
O	0.108182000000	0.964287000000	2.524640000000
S	0.511313000000	2.203962000000	0.743759000000
C	2.315606000000	2.076816000000	0.953326000000
C	2.958469000000	0.973145000000	0.117801000000
N	2.217494000000	-0.282430000000	0.252828000000
H	2.315604000000	-0.669728000000	1.199798000000
H	2.554694000000	-0.991493000000	-0.408557000000
N	-0.655281000000	-2.884186000000	-1.131424000000
C	-0.578054000000	-4.233697000000	-1.119001000000
B	-1.510686000000	-1.968116000000	-2.030559000000
N	0.049392000000	-2.361239000000	-0.107051000000
H	-1.126140000000	-1.418598000000	-4.801838000000
H	-1.100274000000	-4.826890000000	-1.874806000000
H	-4.399740000000	-1.809761000000	-1.846456000000
C	0.212057000000	-4.608068000000	-0.037114000000
N	-2.495453000000	-1.171608000000	-1.146155000000
C	0.581641000000	-3.391059000000	0.578957000000
N	-2.034211000000	-0.311439000000	-0.210081000000
C	-3.847630000000	-1.176117000000	-1.146834000000
N	-0.619929000000	-0.954730000000	-2.790585000000
C	-4.281550000000	-0.285454000000	-0.169953000000
N	0.067081000000	0.019655000000	-2.143055000000
C	-3.099507000000	0.237963000000	0.399737000000
C	-0.605752000000	-0.736721000000	-4.123496000000
C	0.112885000000	0.426996000000	-4.364747000000
C	0.506832000000	0.880259000000	-3.087203000000
C	1.407186000000	-3.197795000000	1.813529000000
C	-2.964574000000	1.222758000000	1.514704000000
C	1.238708000000	2.149251000000	-2.786545000000
H	-2.128309000000	-2.648920000000	-2.839957000000
H	0.480258000000	-5.619292000000	0.280194000000
H	-5.310291000000	-0.036112000000	0.103599000000
H	0.315228000000	0.905500000000	-5.326611000000
H	1.325751000000	-4.085027000000	2.471172000000
H	2.487067000000	-3.070218000000	1.579903000000
H	1.060959000000	-2.311070000000	2.380463000000
H	-3.947013000000	1.670817000000	1.754774000000
H	-2.261644000000	2.038995000000	1.255462000000
H	-2.563662000000	0.740532000000	2.427913000000
H	0.939936000000	2.934921000000	-3.507651000000
H	0.998226000000	2.507457000000	-1.765293000000
H	2.340554000000	2.035220000000	-2.871264000000
H	4.025192000000	0.864380000000	0.419201000000
H	2.947403000000	1.253369000000	-0.950733000000
H	2.478397000000	1.891777000000	2.035438000000
H	2.781842000000	3.054464000000	0.714751000000

Table 8. Cartesian Coordinates (Å) of the DFT-Optimized $\mathbf{B}^{Co,S=1/2}$ Model.

Co	0.012600000000	-0.149879000000	0.022201000000
O	-0.002446000000	-0.203621000000	1.909987000000
O	0.143677000000	1.179416000000	2.484036000000
S	0.598333000000	2.286746000000	1.325902000000
C	2.414900000000	2.003746000000	1.268230000000
C	2.866728000000	0.996020000000	0.222724000000
N	2.017878000000	-0.207113000000	0.221865000000
H	2.034748000000	-0.650099000000	1.146193000000
H	2.364304000000	-0.886658000000	-0.456071000000
N	-0.608799000000	-2.915983000000	-1.006475000000
C	-0.598802000000	-4.262738000000	-0.913982000000
B	-1.455360000000	-2.007410000000	-1.910354000000
N	0.077881000000	-2.364001000000	0.023557000000
H	-0.995856000000	-1.421325000000	-4.686680000000
H	-1.121038000000	-4.870397000000	-1.643225000000
H	-4.320797000000	-1.873874000000	-1.626187000000
C	0.126343000000	-4.605785000000	0.212404000000
N	-2.417790000000	-1.175567000000	-1.030339000000
C	0.525221000000	-3.380206000000	0.780974000000
N	-1.942891000000	-0.277570000000	-0.122827000000
C	-3.764083000000	-1.211002000000	-0.975380000000
N	-0.561154000000	-0.995062000000	-2.663995000000
C	-4.180733000000	-0.312679000000	-0.009599000000
N	0.048377000000	0.008752000000	-1.977996000000
C	-3.003626000000	0.254993000000	0.508418000000
C	-0.534399000000	-0.736348000000	-3.986237000000
C	0.110807000000	0.470127000000	-4.178708000000
C	0.447479000000	0.919214000000	-2.889750000000
C	1.285511000000	-3.162179000000	2.047198000000
C	-2.878584000000	1.277972000000	1.580741000000
C	1.063678000000	2.231387000000	-2.540253000000
H	-2.079538000000	-2.669631000000	-2.702669000000
H	0.330559000000	-5.600397000000	0.589739000000
H	-5.195339000000	-0.085283000000	0.292541000000
H	0.298662000000	0.979176000000	-5.115814000000
H	1.074546000000	-3.969892000000	2.756966000000
H	2.374142000000	-3.158672000000	1.884986000000
H	0.990430000000	-2.213317000000	2.510194000000
H	-3.868971000000	1.548059000000	1.961797000000
H	-2.401061000000	2.193742000000	1.208147000000
H	-2.264697000000	0.904510000000	2.405522000000
H	0.647783000000	3.017617000000	-3.180801000000
H	0.850343000000	2.499092000000	-1.500889000000
H	2.151870000000	2.241075000000	-2.693321000000
H	3.919027000000	0.730148000000	0.415255000000
H	2.819513000000	1.440452000000	-0.774567000000
H	2.677617000000	1.680550000000	2.283659000000
H	2.898386000000	2.972895000000	1.092349000000

Table 9. Cartesian Coordinates (Å) of the DFT-Optimized $\mathbf{B}^{Co,S=3/2}$ Model.

Co	0.028745000000	-0.188278000000	0.174096000000
O	-0.043496000000	-0.137579000000	2.065512000000
O	0.225615000000	1.199641000000	2.637674000000
S	0.719539000000	2.280087000000	1.450079000000
C	2.527662000000	1.946000000000	1.417757000000
C	3.000192000000	1.075224000000	0.265315000000
N	2.233621000000	-0.173669000000	0.174405000000
H	2.413512000000	-0.761854000000	0.989634000000
H	2.513501000000	-0.709449000000	-0.647255000000
N	-0.651639000000	-2.872690000000	-0.967422000000
C	-0.602415000000	-4.218925000000	-0.892869000000
B	-1.512510000000	-1.993754000000	-1.897837000000
N	0.034792000000	-2.321667000000	0.065699000000
H	-1.125682000000	-1.440271000000	-4.675351000000
H	-1.114536000000	-4.829014000000	-1.626981000000
H	-4.404457000000	-1.873321000000	-1.714438000000
C	0.143588000000	-4.561612000000	0.220562000000
N	-2.517045000000	-1.186062000000	-1.046707000000
C	0.519734000000	-3.336659000000	0.801962000000
N	-2.071287000000	-0.299051000000	-0.120724000000
C	-3.865761000000	-1.219718000000	-1.039114000000
N	-0.629703000000	-0.983717000000	-2.672145000000
C	-4.313032000000	-0.329157000000	-0.076915000000
N	0.025026000000	0.016154000000	-2.021962000000
C	-3.148403000000	0.228385000000	0.480831000000
C	-0.626951000000	-0.755628000000	-4.000138000000
C	0.050468000000	0.427094000000	-4.236539000000
C	0.431008000000	0.887757000000	-2.964803000000
C	1.299118000000	-3.111035000000	2.054761000000
C	-3.019201000000	1.232105000000	1.574032000000
C	1.118509000000	2.171774000000	-2.642033000000
H	-2.101593000000	-2.694533000000	-2.684636000000
H	0.376258000000	-5.556395000000	0.580090000000
H	-5.337656000000	-0.106197000000	0.194031000000
H	0.231099000000	0.907049000000	-5.190505000000
H	1.086341000000	-3.903341000000	2.781212000000
H	2.385207000000	-3.130968000000	1.875207000000
H	1.026894000000	-2.150542000000	2.507744000000
H	-4.000690000000	1.472350000000	1.995647000000
H	-2.573037000000	2.166920000000	1.208630000000
H	-2.370171000000	0.852931000000	2.370698000000
H	0.760176000000	2.966903000000	-3.305658000000
H	0.909885000000	2.476791000000	-1.611211000000
H	2.207552000000	2.110889000000	-2.777785000000
H	4.080725000000	0.889074000000	0.388286000000
H	2.871976000000	1.613642000000	-0.678422000000
H	2.734261000000	1.482534000000	2.391480000000
H	3.049636000000	2.910782000000	1.395572000000

Table 10. Cartesian Coordinates (Å) for **TS2** (Co; $S = 1/2$).

Co	0.023578000000	-0.247831000000	0.118382000000
O	-0.047126000000	-0.331089000000	1.920508000000
O	0.179297000000	1.462760000000	2.432685000000
S	0.422095000000	2.121133000000	1.021611000000
C	2.270367000000	2.080853000000	0.898251000000
C	2.828162000000	0.853720000000	0.180825000000
N	1.983450000000	-0.319613000000	0.425817000000
H	1.838435000000	-0.499201000000	1.441880000000
H	2.364702000000	-1.159474000000	-0.025779000000
N	-0.631941000000	-2.883478000000	-1.022671000000
C	-0.563416000000	-4.232766000000	-0.985992000000
B	-1.462809000000	-1.953916000000	-1.923042000000
N	0.024960000000	-2.348525000000	0.025970000000
H	-0.974253000000	-1.345094000000	-4.682862000000
H	-1.056440000000	-4.834983000000	-1.754138000000
H	-4.339550000000	-1.763093000000	-1.688293000000
C	0.173234000000	-4.591289000000	0.137402000000
N	-2.419872000000	-1.134758000000	-1.029633000000
C	0.516067000000	-3.367994000000	0.759269000000
N	-1.934308000000	-0.304186000000	-0.073348000000
C	-3.771005000000	-1.144292000000	-0.988791000000
N	-0.543649000000	-0.941259000000	-2.643014000000
C	-4.177255000000	-0.291092000000	0.029654000000
N	0.089311000000	0.025571000000	-1.935558000000
C	-2.983658000000	0.216990000000	0.590084000000
C	-0.495303000000	-0.673392000000	-3.965426000000
C	0.188587000000	0.521429000000	-4.137245000000
C	0.523629000000	0.941447000000	-2.831178000000
C	1.246351000000	-3.164006000000	2.049910000000
C	-2.839134000000	1.173466000000	1.724215000000
C	1.172799000000	2.245280000000	-2.486039000000
H	-2.090537000000	-2.605649000000	-2.747089000000
H	0.419444000000	-5.598096000000	0.485024000000
H	-5.197085000000	-0.054409000000	0.343819000000
H	0.402214000000	1.047466000000	-5.071317000000
H	1.093692000000	-4.037706000000	2.713018000000
H	2.343480000000	-3.054411000000	1.905617000000
H	0.862967000000	-2.252672000000	2.552814000000
H	-3.803271000000	1.278116000000	2.257189000000
H	-2.539870000000	2.181264000000	1.366641000000
H	-2.051833000000	0.825268000000	2.417930000000
H	0.835502000000	3.022087000000	-3.199358000000
H	0.888495000000	2.583111000000	-1.473170000000
H	2.280588000000	2.210183000000	-2.552367000000
H	3.872089000000	0.668150000000	0.518535000000
H	2.863839000000	1.018437000000	-0.910394000000
H	2.573326000000	2.110271000000	1.962766000000
H	2.617035000000	3.016273000000	0.416347000000

Table 11. Cartesian Coordinates (Å) for **TS2** (Co; *S* = 3/2).

Co	0.012065000000	-0.222121000000	0.237862000000
O	-0.064845000000	-0.170433000000	1.961778000000
O	0.325619000000	1.501488000000	2.631239000000
S	0.800828000000	2.264704000000	1.322011000000
C	2.599887000000	1.866448000000	1.266701000000
C	3.031209000000	0.894670000000	0.172377000000
N	2.232357000000	-0.331232000000	0.173199000000
H	2.396240000000	-0.871631000000	1.031249000000
H	2.476139000000	-0.934214000000	-0.621055000000
N	-0.631071000000	-2.876765000000	-0.945361000000
C	-0.525509000000	-4.224147000000	-0.901733000000
B	-1.487948000000	-1.997183000000	-1.882837000000
N	0.008147000000	-2.326093000000	0.108327000000
H	-1.063584000000	-1.383470000000	-4.645893000000
H	-0.996393000000	-4.842045000000	-1.671342000000
H	-4.399441000000	-1.928880000000	-1.751642000000
C	0.213201000000	-4.563124000000	0.227111000000
N	-2.521488000000	-1.219854000000	-1.041118000000
C	0.523499000000	-3.329501000000	0.844024000000
N	-2.100193000000	-0.320142000000	-0.125234000000
C	-3.874844000000	-1.256052000000	-1.067445000000
N	-0.608629000000	-0.948199000000	-2.616066000000
C	-4.346953000000	-0.344934000000	-0.129395000000
N	0.010931000000	0.048377000000	-1.937346000000
C	-3.185772000000	0.226596000000	0.443957000000
C	-0.591445000000	-0.691708000000	-3.942804000000
C	0.058593000000	0.519528000000	-4.143893000000
C	0.407894000000	0.960059000000	-2.848393000000
C	1.261219000000	-3.082390000000	2.123015000000
C	-3.087742000000	1.294587000000	1.485048000000
C	1.049023000000	2.262843000000	-2.485194000000
H	-2.049328000000	-2.704822000000	-2.709798000000
H	0.483504000000	-5.563339000000	0.575609000000
H	-5.387048000000	-0.113187000000	0.115964000000
H	0.242409000000	1.034117000000	-5.090700000000
H	1.040202000000	-3.882505000000	2.856543000000
H	2.364326000000	-3.078668000000	1.977363000000
H	0.946673000000	-2.110284000000	2.553747000000
H	-3.840131000000	1.135193000000	2.282339000000
H	-3.282054000000	2.296045000000	1.044367000000
H	-2.084177000000	1.302219000000	1.950438000000
H	0.614871000000	3.080974000000	-3.092231000000
H	0.873261000000	2.503204000000	-1.419552000000
H	2.142822000000	2.266121000000	-2.678315000000
H	4.118796000000	0.684255000000	0.300055000000
H	2.916034000000	1.371777000000	-0.818363000000
H	2.787064000000	1.458523000000	2.280832000000
H	3.167164000000	2.814198000000	1.170022000000

Table 12. Cartesian Coordinates (Å) of the DFT-Optimized $\mathbf{C}^{\mathbf{Co},S=1/2}$ Model.

Co	0.034492000000	-0.129903000000	0.097482000000
O	0.026186000000	-0.261611000000	1.825782000000
O	-0.891870000000	2.923270000000	0.961633000000
S	0.161457000000	2.146957000000	0.166954000000
C	1.666770000000	2.122651000000	1.247329000000
C	2.672550000000	1.197384000000	0.603281000000
N	2.019825000000	-0.105909000000	0.324818000000
H	1.978044000000	-0.637167000000	1.198916000000
H	2.523437000000	-0.644195000000	-0.380706000000
N	-0.748570000000	-2.718018000000	-1.124194000000
C	-0.743402000000	-4.064251000000	-1.077683000000
B	-1.651937000000	-1.759204000000	-1.932766000000
N	0.053138000000	-2.215149000000	-0.155290000000
H	-1.290570000000	-1.193963000000	-4.707331000000
H	-1.341736000000	-4.640356000000	-1.772816000000
H	-4.459833000000	-1.608419000000	-1.432037000000
C	0.088644000000	-4.455190000000	-0.043003000000
N	-2.510595000000	-0.963797000000	-0.940521000000
C	0.560151000000	-3.259667000000	0.525820000000
N	-1.937752000000	-0.252526000000	0.072452000000
C	-3.837891000000	-1.066148000000	-0.730428000000
N	-0.749613000000	-0.793245000000	-2.708113000000
C	-4.139294000000	-0.408785000000	0.444310000000
N	0.136852000000	0.000315000000	-2.054175000000
C	-2.916116000000	0.078783000000	0.940396000000
C	-0.649692000000	-0.633036000000	-4.038382000000
C	0.339849000000	0.301059000000	-4.279991000000
C	0.814016000000	0.673370000000	-3.013390000000
C	1.435172000000	-3.104166000000	1.723425000000
C	-2.717860000000	0.789276000000	2.231638000000
C	1.920157000000	1.641267000000	-2.769268000000
H	-2.349876000000	-2.382692000000	-2.692791000000
H	0.319576000000	-5.463505000000	0.277435000000
H	-5.110746000000	-0.285574000000	0.905934000000
H	0.683415000000	0.676241000000	-5.235825000000
H	1.400984000000	-4.013806000000	2.331703000000
H	2.489176000000	-2.939462000000	1.454944000000
H	1.090908000000	-2.264581000000	2.340167000000
H	-3.693604000000	0.986536000000	2.689592000000
H	-2.187803000000	1.736512000000	2.092703000000
H	-2.111631000000	0.175339000000	2.905607000000
H	2.177493000000	2.146323000000	-3.705989000000
H	1.639964000000	2.407720000000	-2.040421000000
H	2.831465000000	1.138018000000	-2.417705000000
H	3.551024000000	1.054100000000	1.248248000000
H	3.029184000000	1.620194000000	-0.339164000000
H	1.333695000000	1.766774000000	2.227524000000
H	2.038143000000	3.151238000000	1.323361000000

Table 13. Cartesian Coordinates (Å) of the DFT-Optimized $\mathbf{C}^{\mathbf{Co},S=3/2}$ Model.

Co	0.031901000000	-0.149600000000	0.233729000000
O	0.106194000000	-0.186507000000	1.900252000000
O	-0.638883000000	2.975352000000	1.284891000000
S	0.332945000000	2.203949000000	0.386857000000
C	1.894492000000	2.055108000000	1.367774000000
C	2.900690000000	1.215580000000	0.601304000000
N	2.309535000000	-0.081783000000	0.214218000000
H	2.429895000000	-0.763126000000	0.961054000000
H	2.747404000000	-0.462709000000	-0.622895000000
N	-0.780366000000	-2.750618000000	-1.059920000000
C	-0.748694000000	-4.097402000000	-1.035000000000
B	-1.685686000000	-1.812524000000	-1.893819000000
N	0.024342000000	-2.249580000000	-0.091553000000
H	-1.359873000000	-1.222591000000	-4.644200000000
H	-1.341984000000	-4.673341000000	-1.734594000000
H	-4.539312000000	-1.749282000000	-1.500873000000
C	0.101653000000	-4.490948000000	-0.015752000000
N	-2.621085000000	-1.049175000000	-0.946971000000
C	0.561070000000	-3.295310000000	0.562207000000
N	-2.108473000000	-0.269480000000	0.040234000000
C	-3.957741000000	-1.159593000000	-0.802452000000
N	-0.787910000000	-0.818214000000	-2.653596000000
C	-4.328455000000	-0.433826000000	0.314262000000
N	0.093360000000	0.000026000000	-2.018025000000
C	-3.132641000000	0.102262000000	0.828236000000
C	-0.720302000000	-0.647730000000	-3.985882000000
C	0.238317000000	0.313334000000	-4.247680000000
C	0.727765000000	0.693195000000	-2.989423000000
C	1.471130000000	-3.131714000000	1.732239000000
C	-2.948675000000	0.903510000000	2.069165000000
C	1.813980000000	1.686411000000	-2.752495000000
H	-2.327360000000	-2.462914000000	-2.681894000000
H	0.353556000000	-5.500508000000	0.284396000000
H	-5.324590000000	-0.302471000000	0.718135000000
H	0.550700000000	0.697974000000	-5.210613000000
H	1.416773000000	-4.013016000000	2.379962000000
H	2.523232000000	-3.028855000000	1.425613000000
H	1.183917000000	-2.253786000000	2.322173000000
H	-3.921069000000	1.121766000000	2.523133000000
H	-2.426606000000	1.846823000000	1.875679000000
H	-2.337024000000	0.349960000000	2.792228000000
H	2.025062000000	2.230217000000	-3.679041000000
H	1.543088000000	2.420564000000	-1.987749000000
H	2.751451000000	1.199610000000	-2.448907000000
H	3.812628000000	1.089051000000	1.204727000000
H	3.200143000000	1.741874000000	-0.310947000000
H	1.602125000000	1.605911000000	2.323781000000
H	2.264751000000	3.073127000000	1.537499000000

Table 14. Cartesian Coordinates (Å) for **TS3** (Co; $S = 1/2$).

Co	0.031028000000	-0.163597000000	0.042289000000
O	0.044132000000	0.164601000000	1.755333000000
O	-0.581592000000	2.919016000000	1.499662000000
S	0.269723000000	2.112839000000	0.547961000000
C	1.948782000000	1.993543000000	1.301113000000
C	2.779706000000	1.025679000000	0.477178000000
N	2.029027000000	-0.227611000000	0.247469000000
H	1.999086000000	-0.752932000000	1.130049000000
H	2.471112000000	-0.807203000000	-0.477284000000
N	-0.700912000000	-2.802048000000	-1.107459000000
C	-0.709459000000	-4.149133000000	-1.002837000000
B	-1.577435000000	-1.856996000000	-1.961381000000
N	0.057196000000	-2.260718000000	-0.134348000000
H	-1.143845000000	-1.331610000000	-4.751011000000
H	-1.286596000000	-4.757680000000	-1.704477000000
H	-4.409492000000	-1.681085000000	-1.570258000000
C	0.077502000000	-4.498925000000	0.090094000000
N	-2.466524000000	-1.044515000000	-0.998415000000
C	0.529384000000	-3.270488000000	0.622333000000
N	-1.930109000000	-0.300821000000	0.005805000000
C	-3.807651000000	-1.117591000000	-0.852141000000
N	-0.671932000000	-0.883845000000	-2.730029000000
C	-4.156160000000	-0.405634000000	0.285731000000
N	0.096512000000	0.005430000000	-2.061111000000
C	-2.940959000000	0.083335000000	0.817755000000
C	-0.574080000000	-0.701531000000	-4.062701000000
C	0.297828000000	0.355968000000	-4.284565000000
C	0.692970000000	0.778642000000	-2.997399000000
C	1.345701000000	-3.043883000000	1.857392000000
C	-2.790661000000	0.848025000000	2.090644000000
C	1.620000000000	1.916274000000	-2.708794000000
H	-2.265587000000	-2.500430000000	-2.742100000000
H	0.287957000000	-5.501360000000	0.472199000000
H	-5.153515000000	-0.248074000000	0.704086000000
H	0.604413000000	0.789388000000	-5.239978000000
H	1.234700000000	-3.901301000000	2.549031000000
H	2.432057000000	-2.946235000000	1.641634000000
H	1.001612000000	-2.130423000000	2.385242000000
H	-3.794077000000	1.070938000000	2.501425000000
H	-2.229226000000	1.790662000000	1.948704000000
H	-2.206967000000	0.262422000000	2.825327000000
H	1.578208000000	2.649517000000	-3.537790000000
H	1.338555000000	2.443122000000	-1.777846000000
H	2.677228000000	1.583450000000	-2.627852000000
H	3.748038000000	0.813704000000	0.980420000000
H	3.018202000000	1.469390000000	-0.505300000000
H	1.781866000000	1.663538000000	2.342115000000
H	2.379632000000	3.015184000000	1.283552000000

Table 15. Cartesian Coordinates (Å) for **TS3** (Co; $S = 3/2$).

Co	0.011585000000	-0.210719000000	0.207521000000
O	0.117168000000	0.136855000000	1.867705000000
O	-0.325960000000	2.935957000000	1.820196000000
S	0.449756000000	2.148952000000	0.796583000000
C	2.137654000000	1.883148000000	1.485741000000
C	2.978438000000	1.054838000000	0.521780000000
N	2.300420000000	-0.197638000000	0.147156000000
H	2.419268000000	-0.901975000000	0.883069000000
H	2.682439000000	-0.589836000000	-0.720742000000
N	-0.725030000000	-2.845534000000	-1.035384000000
C	-0.663219000000	-4.194616000000	-0.987763000000
B	-1.629265000000	-1.933195000000	-1.899105000000
N	0.030495000000	-2.309252000000	-0.055777000000
H	-1.291180000000	-1.327502000000	-4.666908000000
H	-1.224428000000	-4.801206000000	-1.703957000000
H	-4.515391000000	-1.849148000000	-1.586622000000
C	0.166866000000	-4.551840000000	0.070690000000
N	-2.594394000000	-1.168077000000	-0.974214000000
C	0.575199000000	-3.325153000000	0.639683000000
N	-2.107237000000	-0.332028000000	-0.030226000000
C	-3.944220000000	-1.220376000000	-0.897910000000
N	-0.751279000000	-0.910639000000	-2.655076000000
C	-4.347636000000	-0.387806000000	0.140041000000
N	0.029538000000	-0.015827000000	-2.004221000000
C	-3.151252000000	0.151957000000	0.666729000000
C	-0.707261000000	-0.700048000000	-3.987905000000
C	0.137959000000	0.376404000000	-4.227060000000
C	0.576049000000	0.779505000000	-2.947947000000
C	1.441045000000	-3.096913000000	1.839158000000
C	-2.985726000000	1.105314000000	1.803817000000
C	1.512024000000	1.907769000000	-2.650178000000
H	-2.255771000000	-2.611255000000	-2.703465000000
H	0.435590000000	-5.558251000000	0.402137000000
H	-5.365666000000	-0.188557000000	0.485344000000
H	0.400507000000	0.827320000000	-5.187605000000
H	1.319886000000	-3.923392000000	2.566617000000
H	2.521547000000	-3.060311000000	1.576580000000
H	1.160985000000	-2.150136000000	2.343251000000
H	-3.887307000000	1.098247000000	2.446389000000
H	-2.820843000000	2.143066000000	1.449314000000
H	-2.095075000000	0.844211000000	2.407217000000
H	1.439109000000	2.679923000000	-3.440743000000
H	1.274368000000	2.389909000000	-1.683379000000
H	2.570969000000	1.570912000000	-2.623666000000
H	3.979370000000	0.872853000000	0.974219000000
H	3.152994000000	1.634959000000	-0.403760000000
H	1.970354000000	1.396397000000	2.465170000000
H	2.571931000000	2.891736000000	1.636969000000

Table 16. Cartesian Coordinates (Å) of the DFT-Optimized $\mathbf{D}^{\mathbf{Co},S=1/2}$ Model.

Co	-0.018568000000	-0.106258000000	-0.173028000000
O	0.010331000000	0.153294000000	1.748583000000
O	0.390523000000	1.694828000000	3.715834000000
S	0.490792000000	1.626856000000	2.208757000000
C	2.321158000000	1.412038000000	1.909206000000
C	2.646534000000	1.224017000000	0.443925000000
N	1.974842000000	0.025174000000	-0.117756000000
H	2.225775000000	-0.787322000000	0.449527000000
H	2.326438000000	-0.163640000000	-1.057653000000
N	-0.627079000000	-2.908354000000	-0.990058000000
C	-0.574965000000	-4.242546000000	-0.789307000000
B	-1.539997000000	-2.088204000000	-1.915573000000
N	0.105567000000	-2.261239000000	-0.049704000000
H	-1.118622000000	-1.656621000000	-4.760170000000
H	-1.121414000000	-4.919648000000	-1.434894000000
H	-4.401230000000	-1.933727000000	-1.522981000000
C	0.225304000000	-4.476986000000	0.313789000000
N	-2.473492000000	-1.210312000000	-1.049379000000
C	0.623197000000	-3.201165000000	0.758250000000
N	-1.962982000000	-0.250664000000	-0.229693000000
C	-3.816745000000	-1.230359000000	-0.942841000000
N	-0.685354000000	-1.115666000000	-2.765188000000
C	-4.193077000000	-0.257933000000	-0.033789000000
N	-0.026160000000	-0.105736000000	-2.144787000000
C	-2.996165000000	0.340563000000	0.397126000000
C	-0.628655000000	-0.951695000000	-4.100089000000
C	0.092375000000	0.200262000000	-4.364876000000
C	0.445311000000	0.714097000000	-3.106315000000
C	1.445100000000	-2.853734000000	1.954110000000
C	-2.834341000000	1.441860000000	1.385102000000
C	1.162156000000	1.987713000000	-2.807033000000
H	-2.183606000000	-2.812664000000	-2.632727000000
H	0.477399000000	-5.432863000000	0.756316000000
H	-5.194943000000	-0.001274000000	0.286491000000
H	0.319217000000	0.630689000000	-5.332126000000
H	1.268598000000	-3.576330000000	2.758445000000
H	2.525201000000	-2.880302000000	1.741459000000
H	1.168718000000	-1.861070000000	2.328049000000
H	-3.805008000000	1.901527000000	1.598301000000
H	-2.160581000000	2.223721000000	1.016100000000
H	-2.413053000000	1.068418000000	2.325233000000
H	0.970590000000	2.718946000000	-3.599420000000
H	0.814559000000	2.423711000000	-1.863766000000
H	2.252449000000	1.860697000000	-2.746772000000
H	3.736695000000	1.147315000000	0.303902000000
H	2.309761000000	2.095789000000	-0.130143000000
H	2.610347000000	0.553568000000	2.529907000000
H	2.812470000000	2.310230000000	2.301124000000

Table 17. Cartesian Coordinates (Å) of the DFT-Optimized $\mathbf{D}^{\mathbf{Co},S=3/2}$ Model.

Co	0.042162000000	-0.165976000000	-0.068713000000
O	0.032437000000	0.430524000000	1.786555000000
O	0.583773000000	1.824071000000	3.837879000000
S	0.641125000000	1.825516000000	2.328533000000
C	2.447748000000	1.488035000000	1.977827000000
C	2.782207000000	1.348296000000	0.506933000000
N	2.213269000000	0.113344000000	-0.080273000000
H	2.566990000000	-0.694730000000	0.435360000000
H	2.539637000000	0.000551000000	-1.040756000000
N	-0.691870000000	-2.882806000000	-0.986201000000
C	-0.599209000000	-4.219664000000	-0.836956000000
B	-1.619081000000	-2.065704000000	-1.913823000000
N	0.038653000000	-2.258642000000	-0.027693000000
H	-1.279726000000	-1.656439000000	-4.749449000000
H	-1.132297000000	-4.885254000000	-1.505016000000
H	-4.491669000000	-1.943844000000	-1.596686000000
C	0.218142000000	-4.478530000000	0.249769000000
N	-2.577393000000	-1.225511000000	-1.048124000000
C	0.591913000000	-3.214262000000	0.738524000000
N	-2.088994000000	-0.294904000000	-0.185705000000
C	-3.924369000000	-1.259367000000	-0.977617000000
N	-0.771478000000	-1.095037000000	-2.777867000000
C	-4.328123000000	-0.323145000000	-0.041635000000
N	-0.047083000000	-0.105882000000	-2.194415000000
C	-3.141193000000	0.263160000000	0.435286000000
C	-0.741609000000	-0.961952000000	-4.115896000000
C	0.026350000000	0.149678000000	-4.426035000000
C	0.438763000000	0.664157000000	-3.188043000000
C	1.422101000000	-2.884029000000	1.932583000000
C	-2.989161000000	1.325945000000	1.469156000000
C	1.253790000000	1.886055000000	-2.926881000000
H	-2.237683000000	-2.810203000000	-2.633440000000
H	0.496375000000	-5.444990000000	0.651330000000
H	-5.339507000000	-0.087212000000	0.265291000000
H	0.247536000000	0.546896000000	-5.408863000000
H	1.233667000000	-3.602176000000	2.738122000000
H	2.499565000000	-2.931695000000	1.713414000000
H	1.173845000000	-1.885533000000	2.310767000000
H	-3.971542000000	1.662006000000	1.816740000000
H	-2.451840000000	2.197523000000	1.075144000000
H	-2.415994000000	0.959902000000	2.327574000000
H	1.081030000000	2.632197000000	-3.709575000000
H	0.985958000000	2.345081000000	-1.968655000000
H	2.333596000000	1.677139000000	-2.918948000000
H	3.875585000000	1.381017000000	0.373485000000
H	2.372241000000	2.202039000000	-0.050239000000
H	2.685776000000	0.589027000000	2.562581000000
H	2.990954000000	2.334326000000	2.414119000000

Table 18. Cartesian Coordinates (Å) of the DFT-Optimized Fe(II) Complex (*S* = 2).

Fe	0.062374000000	0.094691000000	0.042235000000
S	2.343232000000	0.384479000000	0.078423000000
H	2.721160000000	1.123830000000	-2.219771000000
C	2.760401000000	0.153798000000	-1.701331000000
N	0.428328000000	-0.440947000000	-2.165433000000
N	-0.568839000000	0.436293000000	2.093862000000
H	3.793556000000	-0.205146000000	-1.779645000000
C	1.831578000000	-0.835641000000	-2.381824000000
N	-1.913409000000	0.552389000000	2.272529000000
C	-2.187108000000	0.811188000000	3.567241000000
H	2.079143000000	-0.918311000000	-3.454424000000
C	-0.987931000000	0.869943000000	4.257250000000
N	-2.661279000000	-1.042193000000	0.481399000000
H	1.969102000000	-1.825177000000	-1.929047000000
C	0.006389000000	0.627222000000	3.292642000000
H	-0.844270000000	1.059793000000	5.313646000000
N	-1.431095000000	-1.470441000000	0.093418000000
H	1.740491000000	0.645916000000	4.536453000000
C	1.485054000000	0.579107000000	3.474073000000
N	-2.572710000000	1.470847000000	0.022366000000
H	1.979880000000	1.405071000000	2.948391000000
N	-1.325729000000	1.625345000000	-0.492823000000
H	1.908180000000	-0.347998000000	3.070867000000
H	-3.210167000000	0.932063000000	3.902639000000
C	-1.541889000000	-2.770210000000	-0.227788000000
C	-2.873031000000	-3.184602000000	-0.050860000000
H	-3.283539000000	-4.172876000000	-0.216141000000
C	-3.542277000000	-2.059734000000	0.401649000000
H	-4.577073000000	-1.913667000000	0.686158000000
H	-0.038901000000	4.291731000000	-1.925705000000
H	-0.111734000000	2.916640000000	-3.026491000000
H	0.784331000000	2.783447000000	-1.490446000000
C	-0.361443000000	-3.567536000000	-0.671552000000
H	-0.385591000000	-4.572003000000	-0.234373000000
H	0.571993000000	-3.086047000000	-0.360041000000
H	-0.334183000000	-3.694887000000	-1.763253000000
H	-4.409398000000	2.515433000000	-0.104269000000
C	-1.341958000000	2.726682000000	-1.260549000000
H	-2.966081000000	4.183622000000	-1.755506000000
C	-2.631108000000	3.289220000000	-1.245016000000
C	-3.374425000000	2.463254000000	-0.419610000000
C	-0.113306000000	3.199000000000	-1.963554000000
B	-2.875647000000	0.377209000000	1.079541000000
H	-4.021034000000	0.483557000000	1.443681000000
H	0.209238000000	0.396535000000	-2.707388000000
H	-0.215511000000	-1.165134000000	-2.482293000000

Table 19. Cartesian Coordinates (Å) of the DFT-Optimized $\mathbf{A}^{\mathbf{Fe},S=2}$ Model.

Fe	-0.017633000000	0.018524000000	0.157875000000
O	-0.102619000000	-0.391083000000	2.082831000000
O	0.703071000000	-0.028248000000	3.019899000000
S	0.199318000000	2.329930000000	0.344181000000
C	1.769696000000	2.332383000000	1.291989000000
C	2.779783000000	1.394476000000	0.651662000000
N	2.203873000000	0.039482000000	0.531491000000
H	2.252822000000	-0.422258000000	1.443804000000
H	2.724998000000	-0.529017000000	-0.134560000000
N	-0.813962000000	-2.773249000000	-1.000952000000
C	-0.785969000000	-4.119618000000	-0.961799000000
B	-1.714942000000	-1.860059000000	-1.860160000000
N	0.065170000000	-2.256476000000	-0.103986000000
H	-1.402486000000	-1.384563000000	-4.649923000000
H	-1.431354000000	-4.702840000000	-1.607302000000
H	-4.571065000000	-1.671212000000	-1.526995000000
C	0.142874000000	-4.502826000000	-0.010730000000
N	-2.643272000000	-1.037511000000	-0.939510000000
C	0.653150000000	-3.301659000000	0.508628000000
N	-2.134654000000	-0.201231000000	0.002499000000
C	-3.986629000000	-1.055089000000	-0.854513000000
N	-0.818866000000	-0.909129000000	-2.676060000000
C	-4.368952000000	-0.205758000000	0.170730000000
N	0.065156000000	-0.060830000000	-2.082933000000
C	-3.173123000000	0.310686000000	0.693101000000
C	-0.760838000000	-0.785584000000	-4.015376000000
C	0.190406000000	0.170325000000	-4.319003000000
C	0.687530000000	0.602762000000	-3.079309000000
C	1.694075000000	-3.152256000000	1.567750000000
C	-2.993563000000	1.247964000000	1.835994000000
C	1.751803000000	1.620621000000	-2.857131000000
H	-2.382666000000	-2.532215000000	-2.606694000000
H	0.416837000000	-5.509993000000	0.277792000000
H	-5.374798000000	0.013947000000	0.505597000000
H	0.490818000000	0.518004000000	-5.299415000000
H	1.847439000000	-4.109029000000	2.076924000000
H	2.665973000000	-2.855796000000	1.148148000000
H	1.405325000000	-2.413897000000	2.323008000000
H	-3.967799000000	1.593091000000	2.196056000000
H	-2.391108000000	2.118734000000	1.552210000000
H	-2.468136000000	0.757297000000	2.664284000000
H	1.909597000000	2.201782000000	-3.771497000000
H	1.476632000000	2.303284000000	-2.045989000000
H	2.712181000000	1.151203000000	-2.600654000000
H	3.711022000000	1.379141000000	1.241117000000
H	3.026509000000	1.750223000000	-0.352722000000
H	1.568716000000	2.031953000000	2.327917000000
H	2.165032000000	3.354615000000	1.311190000000

Table 20. Cartesian Coordinates (Å) for **TS1** (Fe; $S = 2$).

Fe	0.029145000000	-0.163256000000	0.236780000000
O	0.027853000000	-0.178918000000	2.199272000000
O	0.099022000000	1.046746000000	2.707202000000
S	0.562595000000	2.223627000000	0.980230000000
C	2.359176000000	2.011159000000	1.198765000000
C	2.991353000000	0.970608000000	0.280029000000
N	2.261991000000	-0.298416000000	0.348853000000
H	2.369243000000	-0.733115000000	1.274132000000
H	2.595393000000	-0.966181000000	-0.356088000000
N	-0.647384000000	-2.853841000000	-0.964813000000
C	-0.597238000000	-4.203667000000	-0.938644000000
B	-1.511145000000	-1.941938000000	-1.867868000000
N	0.060311000000	-2.340482000000	0.066161000000
H	-1.152378000000	-1.395440000000	-4.644834000000
H	-1.127760000000	-4.792930000000	-1.691857000000
H	-4.399798000000	-1.843577000000	-1.694944000000
C	0.176632000000	-4.587781000000	0.152326000000
N	-2.515157000000	-1.153587000000	-0.992259000000
C	0.564131000000	-3.376778000000	0.765812000000
N	-2.084125000000	-0.274451000000	-0.056634000000
C	-3.866786000000	-1.184764000000	-1.003710000000
N	-0.636334000000	-0.924655000000	-2.636175000000
C	-4.330593000000	-0.291788000000	-0.043287000000
N	0.046316000000	0.057298000000	-1.995159000000
C	-3.166887000000	0.263070000000	0.534256000000
C	-0.632059000000	-0.709160000000	-3.970767000000
C	0.078623000000	0.457680000000	-4.218491000000
C	0.477278000000	0.915788000000	-2.943313000000
C	1.379069000000	-3.184691000000	2.007201000000
C	-3.067813000000	1.311076000000	1.595433000000
C	1.216070000000	2.180516000000	-2.640512000000
H	-2.122110000000	-2.636916000000	-2.670320000000
H	0.421087000000	-5.602793000000	0.476521000000
H	-5.368348000000	-0.062986000000	0.213930000000
H	0.274049000000	0.933327000000	-5.183197000000
H	1.227393000000	-4.034552000000	2.700822000000
H	2.468422000000	-3.140455000000	1.786898000000
H	1.080629000000	-2.251498000000	2.526056000000
H	-3.834180000000	1.143582000000	2.377585000000
H	-3.250203000000	2.319676000000	1.166531000000
H	-2.072373000000	1.318509000000	2.080577000000
H	0.896435000000	2.981751000000	-3.335058000000
H	1.010269000000	2.517085000000	-1.604519000000
H	2.314519000000	2.066343000000	-2.763170000000
H	4.063823000000	0.849154000000	0.555559000000
H	2.960740000000	1.320535000000	-0.767862000000
H	2.484758000000	1.720418000000	2.262593000000
H	2.861724000000	2.989668000000	1.059422000000

Table 21. Cartesian Coordinates (Å) of the DFT-Optimized $\mathbf{B}^{\mathbf{Fe},S=2}$ Model.

Fe	0.017430000000	-0.161694000000	0.195646000000
O	0.043236000000	0.005410000000	2.121654000000
O	0.255691000000	1.427480000000	2.561507000000
S	0.805458000000	2.367817000000	1.291982000000
C	2.606050000000	1.985487000000	1.313804000000
C	3.080182000000	1.020253000000	0.238784000000
N	2.292660000000	-0.217645000000	0.228153000000
H	2.395423000000	-0.711964000000	1.115875000000
H	2.613778000000	-0.843878000000	-0.510100000000
N	-0.645550000000	-2.842453000000	-0.987013000000
C	-0.626602000000	-4.187511000000	-0.909165000000
B	-1.502174000000	-1.950780000000	-1.916980000000
N	0.034040000000	-2.306996000000	0.062285000000
H	-1.119358000000	-1.394446000000	-4.685806000000
H	-1.138590000000	-4.788252000000	-1.651248000000
H	-4.389293000000	-1.889274000000	-1.766345000000
C	0.089507000000	-4.547949000000	0.220261000000
N	-2.528163000000	-1.168154000000	-1.064190000000
C	0.479159000000	-3.333556000000	0.810327000000
N	-2.115499000000	-0.309654000000	-0.093795000000
C	-3.874700000000	-1.245356000000	-1.063329000000
N	-0.623180000000	-0.934612000000	-2.682607000000
C	-4.355908000000	-0.416126000000	-0.063544000000
N	0.038140000000	0.063542000000	-2.034426000000
C	-3.213239000000	0.150959000000	0.527891000000
C	-0.616327000000	-0.711337000000	-4.012238000000
C	0.072579000000	0.463386000000	-4.251777000000
C	0.456211000000	0.924943000000	-2.981077000000
C	1.227138000000	-3.115170000000	2.082860000000
C	-3.119617000000	1.108986000000	1.665294000000
C	1.166590000000	2.197174000000	-2.662504000000
H	-2.081556000000	-2.650592000000	-2.712074000000
H	0.290283000000	-5.548561000000	0.582723000000
H	-5.388899000000	-0.242577000000	0.211555000000
H	0.260971000000	0.937147000000	-5.207322000000
H	0.965643000000	-3.888524000000	2.813755000000
H	2.316231000000	-3.172864000000	1.935906000000
H	0.975848000000	-2.138586000000	2.514815000000
H	-4.036308000000	1.084563000000	2.263940000000
H	-2.981294000000	2.139807000000	1.310801000000
H	-2.267627000000	0.859977000000	2.306948000000
H	0.816020000000	3.000218000000	-3.320757000000
H	0.973670000000	2.502157000000	-1.628791000000
H	2.253064000000	2.116807000000	-2.807917000000
H	4.154823000000	0.826583000000	0.399314000000
H	2.981895000000	1.486682000000	-0.746786000000
H	2.781419000000	1.587023000000	2.322002000000
H	3.156122000000	2.931109000000	1.231175000000

Table 22. Cartesian Coordinates (Å) for **TS2** (Fe; $S = 2$).

Fe	-0.018981000000	-0.160745000000	0.234151000000
O	0.008067000000	-0.059847000000	2.036267000000
O	0.334266000000	1.513762000000	2.603079000000
S	0.884512000000	2.335394000000	1.331956000000
C	2.665439000000	1.870255000000	1.309323000000
C	3.087974000000	0.910195000000	0.200638000000
N	2.265778000000	-0.301363000000	0.171434000000
H	2.380682000000	-0.834534000000	1.042188000000
H	2.534598000000	-0.913509000000	-0.607850000000
N	-0.629491000000	-2.845869000000	-0.961330000000
C	-0.541703000000	-4.193392000000	-0.908464000000
B	-1.499213000000	-1.972447000000	-1.899530000000
N	0.012097000000	-2.298873000000	0.096789000000
H	-1.102363000000	-1.381573000000	-4.673076000000
H	-1.019434000000	-4.810385000000	-1.674825000000
H	-4.407084000000	-1.976338000000	-1.743891000000
C	0.188821000000	-4.538321000000	0.225035000000
N	-2.546047000000	-1.209540000000	-1.053415000000
C	0.508843000000	-3.307368000000	0.839761000000
N	-2.145930000000	-0.311580000000	-0.124613000000
C	-3.896214000000	-1.294502000000	-1.058140000000
N	-0.638977000000	-0.924047000000	-2.648643000000
C	-4.389404000000	-0.417105000000	-0.097080000000
N	-0.001947000000	0.071349000000	-1.985271000000
C	-3.243291000000	0.183270000000	0.472555000000
C	-0.618623000000	-0.687792000000	-3.979824000000
C	0.054819000000	0.507654000000	-4.198924000000
C	0.414621000000	0.958991000000	-2.909640000000
C	1.238786000000	-3.054964000000	2.121713000000
C	-3.154258000000	1.226371000000	1.539097000000
C	1.100159000000	2.241452000000	-2.555835000000
H	-2.061360000000	-2.692406000000	-2.715548000000
H	0.444652000000	-5.541327000000	0.576475000000
H	-5.434105000000	-0.229778000000	0.165974000000
H	0.249257000000	1.003066000000	-5.153800000000
H	0.990825000000	-3.835291000000	2.867747000000
H	2.342723000000	-3.082093000000	1.985270000000
H	0.944767000000	-2.065218000000	2.529933000000
H	-3.894774000000	1.033043000000	2.339634000000
H	-3.369093000000	2.235806000000	1.127403000000
H	-2.144192000000	1.236911000000	1.992512000000
H	0.707330000000	3.069712000000	-3.177237000000
H	0.925885000000	2.499580000000	-1.493599000000
H	2.195656000000	2.196434000000	-2.734861000000
H	4.170226000000	0.676066000000	0.335555000000
H	2.992630000000	1.408513000000	-0.782628000000
H	2.819925000000	1.432859000000	2.316809000000
H	3.268517000000	2.798522000000	1.246194000000

Table 23. Cartesian Coordinates (Å) of the DFT-Optimized $\mathbf{C}^{\mathbf{Fe},S=2}$ Model.

Fe	0.004621000000	-0.116463000000	0.205832000000
O	0.077505000000	-0.164225000000	1.873543000000
O	-0.572091000000	2.980557000000	1.326757000000
S	0.438191000000	2.280944000000	0.402945000000
C	1.969890000000	2.030204000000	1.407135000000
C	2.960472000000	1.176190000000	0.636107000000
N	2.351681000000	-0.110875000000	0.243098000000
H	2.408378000000	-0.772568000000	1.015547000000
H	2.831194000000	-0.525469000000	-0.554615000000
N	-0.774220000000	-2.749987000000	-1.088478000000
C	-0.785261000000	-4.095895000000	-1.034964000000
B	-1.684268000000	-1.810987000000	-1.920543000000
N	0.033219000000	-2.256180000000	-0.114412000000
H	-1.339619000000	-1.211058000000	-4.668127000000
H	-1.389884000000	-4.667167000000	-1.728738000000
H	-4.546571000000	-1.758559000000	-1.528366000000
C	0.039311000000	-4.496978000000	0.002716000000
N	-2.631647000000	-1.055736000000	-0.972785000000
C	0.525393000000	-3.306753000000	0.567606000000
N	-2.127215000000	-0.268723000000	0.014959000000
C	-3.967460000000	-1.161903000000	-0.833671000000
N	-0.793823000000	-0.805050000000	-2.670785000000
C	-4.346735000000	-0.422915000000	0.273825000000
N	0.079925000000	0.015997000000	-2.025455000000
C	-3.156878000000	0.114846000000	0.794622000000
C	-0.709797000000	-0.634505000000	-4.001945000000
C	0.250955000000	0.327367000000	-4.252236000000
C	0.726528000000	0.708734000000	-2.989295000000
C	1.418479000000	-3.144047000000	1.750089000000
C	-2.971318000000	0.936283000000	2.021058000000
C	1.813905000000	1.696356000000	-2.738755000000
H	-2.320684000000	-2.461876000000	-2.711748000000
H	0.256754000000	-5.508477000000	0.322349000000
H	-5.346563000000	-0.286383000000	0.666435000000
H	0.574476000000	0.711703000000	-5.211468000000
H	1.330106000000	-4.010775000000	2.413401000000
H	2.477538000000	-3.071816000000	1.460061000000
H	1.139153000000	-2.246525000000	2.314653000000
H	-2.457958000000	0.350193000000	2.793701000000
H	-3.942433000000	1.260389000000	2.410035000000
H	-2.345882000000	1.817091000000	1.834470000000
H	2.045502000000	2.233624000000	-3.664161000000
H	1.535724000000	2.433743000000	-1.979851000000
H	2.739936000000	1.201659000000	-2.414752000000
H	3.870804000000	1.032926000000	1.239003000000
H	3.268222000000	1.700221000000	-0.275336000000
H	1.633901000000	1.559170000000	2.338366000000
H	2.383920000000	3.022698000000	1.621641000000

Table 24. Cartesian Coordinates (Å) for **TS3** (Fe; $S = 2$).

Fe	0.000180000000	-0.165333000000	0.255505000000
O	0.107455000000	0.169646000000	1.930724000000
O	-0.105130000000	2.869199000000	2.088135000000
S	0.585118000000	2.189995000000	0.932194000000
C	2.292571000000	1.778080000000	1.489386000000
C	3.034159000000	0.962729000000	0.439623000000
N	2.303061000000	-0.269892000000	0.103762000000
H	2.454606000000	-0.981709000000	0.827689000000
H	2.614488000000	-0.667553000000	-0.789645000000
N	-0.663595000000	-2.855412000000	-1.023384000000
C	-0.620521000000	-4.204564000000	-0.951408000000
B	-1.566933000000	-1.955557000000	-1.903905000000
N	0.061239000000	-2.315890000000	-0.020632000000
H	-1.195966000000	-1.368927000000	-4.671451000000
H	-1.164683000000	-4.816087000000	-1.676640000000
H	-4.462760000000	-1.916930000000	-1.646698000000
C	0.164658000000	-4.556874000000	0.142610000000
N	-2.567170000000	-1.203762000000	-0.996738000000
C	0.563813000000	-3.327688000000	0.712202000000
N	-2.120338000000	-0.341848000000	-0.053864000000
C	-3.917293000000	-1.265134000000	-0.958294000000
N	-0.708955000000	-0.911566000000	-2.653644000000
C	-4.362434000000	-0.409327000000	0.044989000000
N	0.008151000000	0.034353000000	-1.999476000000
C	-3.189778000000	0.154960000000	0.595735000000
C	-0.660210000000	-0.704435000000	-3.987893000000
C	0.119332000000	0.421206000000	-4.222551000000
C	0.513961000000	0.858964000000	-2.939863000000
C	1.372349000000	-3.079780000000	1.947406000000
C	-3.053265000000	1.162410000000	1.689801000000
C	1.356567000000	2.054286000000	-2.624019000000
H	-2.170711000000	-2.648611000000	-2.712719000000
H	0.407758000000	-5.561966000000	0.496920000000
H	-5.394113000000	-0.211979000000	0.348379000000
H	0.363925000000	0.881928000000	-5.183201000000
H	1.168745000000	-3.860525000000	2.706104000000
H	2.466716000000	-3.107802000000	1.748168000000
H	1.107277000000	-2.094624000000	2.383177000000
H	-3.853170000000	1.029629000000	2.444215000000
H	-3.133807000000	2.196832000000	1.293387000000
H	-2.064847000000	1.077692000000	2.182237000000
H	1.179855000000	2.852928000000	-3.370793000000
H	1.119836000000	2.466471000000	-1.624636000000
H	2.442178000000	1.816613000000	-2.657878000000
H	4.067188000000	0.753070000000	0.798147000000
H	3.136808000000	1.558486000000	-0.487385000000
H	2.139709000000	1.238198000000	2.443796000000
H	2.799347000000	2.745099000000	1.681894000000

Table 25. Cartesian Coordinates (Å) of the DFT-Optimized $\mathbf{D}^{\mathbf{Fe},S=2}$ Model.

Fe	-0.035392000000	-0.094305000000	0.039480000000
O	0.116901000000	0.919402000000	1.660063000000
O	0.985166000000	2.168468000000	3.698573000000
S	1.053482000000	2.133708000000	2.191421000000
C	2.724490000000	1.361836000000	1.865304000000
C	3.005865000000	1.075864000000	0.403623000000
N	2.254162000000	-0.096377000000	-0.083543000000
H	2.563051000000	-0.930104000000	0.418602000000
H	2.465106000000	-0.266091000000	-1.067699000000
N	-0.629892000000	-2.858495000000	-0.938870000000
C	-0.527744000000	-4.197441000000	-0.803996000000
B	-1.540478000000	-2.055479000000	-1.900899000000
N	0.037699000000	-2.241858000000	0.072025000000
H	-1.155337000000	-1.594636000000	-4.711474000000
H	-1.012219000000	-4.858736000000	-1.511996000000
H	-4.423785000000	-2.069540000000	-1.751842000000
C	0.227578000000	-4.465047000000	0.324172000000
N	-2.581476000000	-1.272941000000	-1.075611000000
C	0.558062000000	-3.203987000000	0.852063000000
N	-2.194172000000	-0.322783000000	-0.180600000000
C	-3.929552000000	-1.362740000000	-1.096388000000
N	-0.706528000000	-1.033885000000	-2.724280000000
C	-4.436164000000	-0.450050000000	-0.190281000000
N	-0.062347000000	0.001820000000	-2.121135000000
C	-3.309174000000	0.187680000000	0.364677000000
C	-0.675161000000	-0.873617000000	-4.061310000000
C	0.008714000000	0.296782000000	-4.346354000000
C	0.371761000000	0.821572000000	-3.095684000000
C	1.314160000000	-2.881901000000	2.097957000000
C	-3.268772000000	1.279425000000	1.379128000000
C	1.089277000000	2.095919000000	-2.799435000000
H	-2.091093000000	-2.816266000000	-2.657554000000
H	0.493585000000	-5.435108000000	0.725328000000
H	-5.476046000000	-0.261592000000	0.046388000000
H	0.207600000000	0.724652000000	-5.321015000000
H	1.010148000000	-3.547441000000	2.913724000000
H	2.398763000000	-3.012891000000	1.971121000000
H	1.117125000000	-1.853699000000	2.422176000000
H	-3.966891000000	1.073508000000	2.198922000000
H	-3.563538000000	2.238993000000	0.932214000000
H	-2.264560000000	1.388580000000	1.799294000000
H	0.784806000000	2.878287000000	-3.503173000000
H	0.861321000000	2.451030000000	-1.788215000000
H	2.179640000000	1.990136000000	-2.889428000000
H	4.091534000000	0.949507000000	0.257173000000
H	2.705675000000	1.940413000000	-0.205173000000
H	2.754526000000	0.463700000000	2.496865000000
H	3.445493000000	2.084726000000	2.265128000000