

Supplementary Information for

X-ray Crystallographic Evidence for the Simultaneous Presence of Axial and Rhombic Sites in Cupredoxins: Atomic Resolution X-ray Crystal Structure Analysis of Pseudoazurin and DFT Modelling

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Figure S1. $2F_o - F_c$ and $F_o - F_c$ ρ density maps as a function of occupancy of Cu positions.2

Table S1. Cu-Ligand distances between oxidized and reduced form of $[N_2S_2]$ type 1 Cu site3-4

Atomic positional coordinates for computational active site model structures

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Selection of final structure model in given crystallographic analysis

The final structure model was selected based on disappearing of F_o-F_c residual density map in Figure S1. The F_o-F_c density map was minimized when the occupancy of positions1 and positions2 is 40 % and 60 %, respectively.

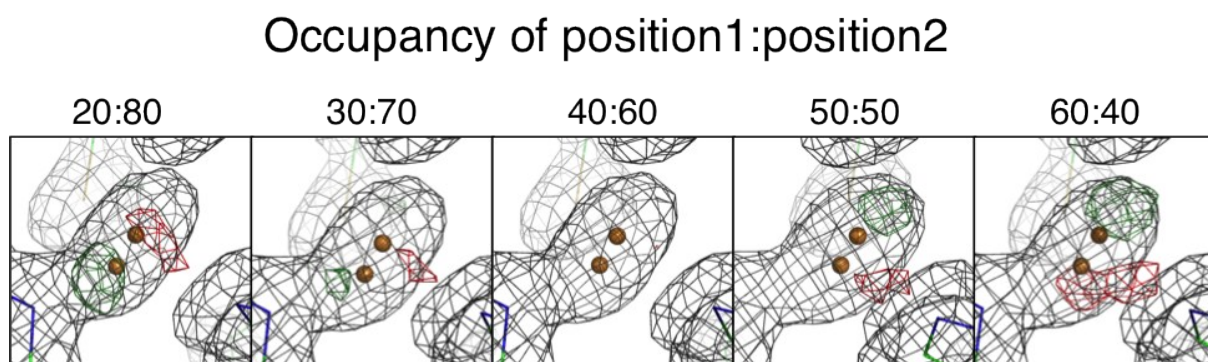


Figure S1: $2F_o-F_c$ (gray: 1.5 σ) and F_o-F_c (green: 4.0 σ , red: -4.0 σ) density maps as a function of occupancy of position1:position2 for Cu ion.

Table S1. Cu-Ligand distances between oxidized and reduced form of [N₂S₂] type 1 Cu site

#1. PlastocyaninA pH 6			
Cu-Ligand	oxidized /	reduced / Å	elongation due to reduction / Å
Cu-N(His37)	1.94	1.91	-0.03
Cu-S(Cys84)	2.16	2.15	-0.01
Cu-N(His87)	1.99	2.54	0.55
Cu-S(Met92)	2.78	2.62	-0.16
PDB ID - resolution	4DP9 - 1.00	4DPA - 1.05	
#2. PlastocyaninB pH 6			
Cu-Ligand	oxidized /	reduced / Å	elongation due to reduction / Å
Cu-N(His37)	2.07	2.06	-0.01
Cu-S(Cys84)	2.14	2.15	0.01
Cu-N(His87)	2.11	2.19	0.08
Cu-S(Met92)	2.74	2.71	-0.03
PDB ID - resolution	4DP2 - 1.80	4DP4 - 1.54	
#3. PlastocyaninA pH 8			
Cu-Ligand	oxidized /	reduced / Å	elongation due to reduction / Å
Cu-N(His37)	1.97	1.98	0.01
Cu-S(Cys84)	2.17	2.18	0.01
Cu-N(His87)	2.02	2.1	0.08
Cu-S(Met92)	2.76	2.71	-0.05
PDB ID - resolution	4DPB - 1.00	4DPC - 1.06	
#4. PlastocyaninB pH 8			
Cu-Ligand	oxidized /	reduced / Å	elongation due to reduction / Å
Cu-N(His37)	2.04	2.04	0.00
Cu-S(Cys84)	2.38	2.2	-0.18
Cu-N(His87)	2.24	2.21	-0.03
Cu-S(Met92)	2.78	2.74	-0.04
PDB ID - resolution	4DP5 - 1.88	4DP6 - 1.67	
#5. Pseudoazurin pH6.0			
Cu-Ligand	oxidized /	reduced / Å	elongation due to reduction / Å
Cu-N(His40)	1.95	2.04	0.09
Cu-S(Cys78)	2.13	2.19	0.06
Cu-N(His81)	1.92	2.11	0.19
Cu-S(Met86)	2.71	2.85	0.14
PDB ID - resolution	1BQK - 1.35	1BQR - 1.60	
#6. Pseudoazurin pH 6.0			
Cu-Ligand	oxidized /	reduced / Å	elongation due to reduction / Å
Cu-N(His40)	1.88	2.23	0.35
Cu-S(Cys78)	2.14	2.24	0.10
Cu-N(His81)	1.99	2.36	0.37
Cu-S(Met86)	2.71	2.76	0.05
PDB ID - resolution	1ZIA - 1.54	1ZIB - 2.00	
#7. Pseudoazurin pH7.0			
Cu-Ligand	oxidized /	reduced / Å	elongation due to reduction / Å
Cu-N(His40)	2.01	2.1	0.09
Cu-S(Cys78)	2.13	2.17	0.04
Cu-N(His81)	2.01	2.31	0.30
Cu-S(Met86)	2.71	2.82	0.11
PDB ID - resolution	8PAZ - 1.60	3PAZ - 1.73	

Table S1. continued

#8. Pseudoazurin pH7.8			
Cu-Ligand	oxidized /	reduced / Å	elongation due to reduction / Å
Cu-N(His40)	2.16	2.16	0.00
Cu-S(Cys78)	2.16	2.17	0.01
Cu-N(His81)	2.12	2.29	0.17
Cu-S(Met86)	2.76	2.91	0.15
PDB ID - resolution	1PAZ - 1.55	1PZA - 1.80	
#9. Pseudoazurin P80I			
Cu-Ligand	oxidized /	reduced / Å	elongation due to reduction / Å
Cu-N(His40)	2.01	2.04	0.03
Cu-S(Cys78)	2.13	2.15	0.02
Cu-N(His81)	2.07	2.13	0.06
Cu-S(Met86)	2.9	2.95	0.05
PDB ID - resolution	6PAZ- 1.91	7PAZ- 2.00	
#10. Pseudoazurin P80A			
Cu-Ligand	oxidized /	reduced / Å	elongation due to reduction / Å
Cu-N(His40)	1.98	2.06	0.08
Cu-S(Cys78)	2.14	2.19	0.05
Cu-N(His81)	1.96	2.02	0.06
Cu-S(Met86)	2.76	3.00	0.24
PDB ID - resolution	4PAZ- 1.76	5PAZ- 1.76	
#11. Amicyanin P94F pH 5.6			
Cu-Ligand	oxidized /	reduced / Å	elongation due to reduction / Å
Cu-N(His53)	1.97	1.98	0.01
Cu-S(Cys92)	2.22	2.2	-0.02
Cu-N(His95)	2.05	2.04	-0.01
Cu-S(Met98)	2.8	2.92	0.12
PDB ID - resolution	1SFD - 0.99	1SFH- 1.05	
#12. Pseudoazurin with engineered Amicyanin pH 7.5			
Cu-Ligand	oxidized /	reduced / Å	elongation due to reduction / Å
Cu-N(His40)	2.09	2.05	-0.04
Cu-S(Cys78)	2.22	2.1	-0.12
Cu-N(His81)	2.09	2.5	0.41
Cu-S(Met86)	2.39	2.37	-0.02
PDB ID - resolution	2UX6- 1.30	2UX7- 1.30	
#13 Pseudoazurin with engineered Amicyanin pH 5.5			
Cu-Ligand	oxidized /	reduced / Å	elongation due to reduction / Å
Cu-N(His40)	2.1	2.16	0.06
Cu-S(Cys78)	2.27	2.14	-0.13
Cu-N(His81)	2.24	2.64	0.4
Cu-S(Met86)	2.38	2.43	0.05
PDB ID - resolution	2UXF - 2.00	2UXG- 1.99	

Fully optimized oxidized site at BP86/def2TZVP level (Fig. 3A)

Cu	7.252537000	9.614021000	19.965134000
H	10.992664000	13.094688000	18.455666000
C	10.928016000	12.269996000	19.184987000
C	9.601964000	11.658014000	19.143017000
S	9.372542000	10.238205000	20.306258000
H	11.727899000	11.553663000	18.938882000
H	11.165197000	12.695300000	20.173366000
H	8.810842000	12.391050000	19.358848000
H	9.395475000	11.257477000	18.139451000
H	6.142258000	7.962957000	25.106638000
C	6.782999000	8.530997000	24.395004000
O	7.647998000	8.001002000	23.719996000
N	6.529990000	9.838997000	24.398997000
C	7.161018000	10.725020000	23.456007000
C	6.115037000	11.431956000	22.615922000
C	5.128137000	10.520717000	21.948447000
N	5.462014000	9.689979000	20.878227000
C	4.362566000	9.004121000	20.553693000
N	3.342589000	9.357861000	21.369862000
C	3.801852000	10.310804000	22.257465000
C	7.986984000	11.822002000	24.160028000
O	7.801008000	12.125001000	25.327015000
H	5.839202000	10.214385000	25.045828000
H	7.815562000	10.103520000	22.828420000
H	5.551324000	12.133944000	23.252313000
H	6.620233000	12.045785000	21.852285000
H	4.275241000	8.277322000	19.753177000
H	3.162413000	10.749090000	23.015275000
H	2.396344000	8.985952000	21.327865000
N	8.919997000	12.348002000	23.379996000
C	9.633998000	13.533000000	23.847998000
H	10.273518000	13.294221000	24.710461000
H	10.264010000	13.914225000	23.035707000
H	9.090916000	11.970963000	22.446404000

H	8.922852000	14.314566000	24.150278000
H	12.314347000	6.916541000	20.072871000
C	11.839011000	6.636991000	19.102015000
O	12.047000000	5.578995000	18.556995000
N	11.049998000	7.563047000	18.630992000
C	10.281002000	7.367926000	17.415968000
C	8.829989000	7.749063000	17.596066000
C	8.148126000	6.981882000	18.693083000
N	7.496928000	7.619876000	19.746348000
C	7.066096000	6.672857000	20.583627000
N	7.403554000	5.454342000	20.102401000
C	8.084404000	5.622033000	18.911967000
H	10.716154000	7.957818000	16.590659000
H	10.868716000	8.406021000	19.187424000
H	10.385308000	6.310246000	17.139609000
H	8.742240000	8.819175000	17.836643000
H	8.308395000	7.601346000	16.636134000
H	6.565566000	6.837741000	21.531421000
H	8.463046000	4.779746000	18.344585000
H	7.206981000	4.565722000	20.557102000
H	8.850376000	10.668739000	13.732614000
C	8.241982000	11.328018000	14.370980000
C	7.950010000	10.700971000	15.672042000
C	7.132892000	11.645766000	16.566226000
S	6.247276000	10.799392000	17.965926000
C	5.320599000	12.251199000	18.604490000
H	8.800737000	12.272471000	14.479369000
H	7.320498000	11.558927000	13.812240000
H	7.381854000	9.766874000	15.523517000
H	8.882224000	10.416063000	16.186323000
H	7.755687000	12.449995000	16.983770000
H	6.323737000	12.107638000	15.979521000
H	4.715089000	11.908762000	19.450313000
H	4.664434000	12.630456000	17.811304000
H	6.011974000	13.035199000	18.936430000

Fully optimized oxidized site at B3LYP/def2TZVP level (Fig. 3B)

Cu	7.281578000	9.592163000	20.010296000
H	10.994097000	13.084257000	18.456958000
C	10.928015000	12.269994000	19.184996000
C	9.601955000	11.658012000	19.143013000
S	9.395072000	10.257244000	20.328480000
H	11.719662000	11.555310000	18.946838000
H	11.159316000	12.695780000	20.165051000
H	8.819162000	12.387715000	19.351371000
H	9.404452000	11.252666000	18.151903000
H	6.150997000	7.963262000	25.095547000
C	6.783004000	8.530991000	24.395012000
O	7.647998000	8.001003000	23.719986000
N	6.529979000	9.838997000	24.399016000
C	7.160989000	10.725013000	23.456043000
C	6.115108000	11.431954000	22.615809000
C	5.129466000	10.523217000	21.950191000
N	5.467186000	9.672038000	20.906293000
C	4.371673000	9.004033000	20.577664000
N	3.348431000	9.385078000	21.360470000
C	3.805392000	10.343719000	22.235082000
C	7.986973000	11.821999000	24.160045000
O	7.801016000	12.125001000	25.327021000
H	5.842913000	10.207441000	25.039501000
H	7.816228000	10.114999000	22.839554000
H	5.555138000	12.122147000	23.252160000
H	6.612449000	12.048294000	21.863195000
H	4.288027000	8.268589000	19.796098000
H	3.165880000	10.803233000	22.967507000
H	2.405467000	9.029027000	21.307785000
N	8.919991000	12.348003000	23.379995000
C	9.633995000	13.533003000	23.847996000
H	10.252299000	13.298878000	24.715381000
H	10.274159000	13.896952000	23.047180000
H	9.091036000	11.975127000	22.456154000

H	8.929274000	14.316540000	24.126987000
H	12.313119000	6.907802000	20.061532000
C	11.839010000	6.636983000	19.102009000
O	12.047001000	5.578984000	18.556995000
N	11.050000000	7.563068000	18.630996000
C	10.281015000	7.367954000	17.416005000
C	8.829961000	7.749019000	17.596025000
C	8.148509000	6.975690000	18.685371000
N	7.511327000	7.599023000	19.747398000
C	7.082500000	6.649910000	20.565908000
N	7.403374000	5.443953000	20.069738000
C	8.076066000	5.624506000	18.882732000
H	10.711563000	7.957327000	16.600656000
H	10.884717000	8.400621000	19.179330000
H	10.380857000	6.321164000	17.138276000
H	8.747880000	8.808686000	17.830434000
H	8.316098000	7.600705000	16.642721000
H	6.587075000	6.802900000	21.508688000
H	8.445081000	4.795999000	18.305325000
H	7.202992000	4.558165000	20.509476000
H	8.871799000	10.686481000	13.749901000
C	8.242004000	11.328047000	14.370977000
C	7.949952000	10.700941000	15.672082000
C	7.103079000	11.636487000	16.541098000
S	6.215842000	10.795018000	17.930640000
C	5.292542000	12.242195000	18.573108000
H	8.769092000	12.280302000	14.482711000
H	7.328171000	11.528308000	13.805147000
H	7.409209000	9.762182000	15.520837000
H	8.875253000	10.445073000	16.192760000
H	7.704159000	12.446047000	16.954852000
H	6.308226000	12.077957000	15.938024000
H	4.674833000	11.900362000	19.398574000
H	4.655953000	12.635133000	17.782830000
H	5.978727000	13.011471000	18.921649000

Fully optimized oxidized site at B38HFP86/def2TZVP level (Fig. 3C)

Cu	7.353587000	9.617781000	20.015001000
H	10.998264000	13.087064000	18.464310000
C	10.928009000	12.270007000	19.184999000
C	9.601979000	11.658003000	19.142994000
S	9.439667000	10.276548000	20.329430000
H	11.713315000	11.552370000	18.944768000
H	11.156186000	12.683223000	20.168606000
H	8.825390000	12.389745000	19.359823000
H	9.399352000	11.260051000	18.150794000
H	6.154164000	7.963556000	25.092336000
C	6.783001000	8.530996000	24.395000000
O	7.648001000	8.000999000	23.719998000
N	6.529997000	9.839008000	24.399000000
C	7.160996000	10.725000000	23.456013000
C	6.115001000	11.431999000	22.615995000
C	5.177572000	10.509787000	21.917150000
N	5.555652000	9.678874000	20.880194000
C	4.487598000	8.999401000	20.519533000
N	3.446860000	9.350052000	21.271873000
C	3.858204000	10.301436000	22.162506000
C	7.987000000	11.821994000	24.160001000
O	7.801001000	12.124999000	25.327002000
H	5.839926000	10.205575000	25.030589000
H	7.819646000	10.116390000	22.840572000
H	5.527114000	12.089989000	23.257379000
H	6.613133000	12.075513000	21.888474000
H	4.440062000	8.271915000	19.729064000
H	3.192924000	10.741936000	22.881320000
H	2.516806000	8.976787000	21.190650000
N	8.920006000	12.348004000	23.379994000
C	9.633996000	13.533000000	23.848000000
H	10.264105000	13.293369000	24.702476000
H	10.257364000	13.906271000	23.041339000
H	9.099582000	11.960587000	22.466055000

H	8.926011000	14.304596000	24.142087000
H	12.311664000	6.905033000	20.058117000
C	11.839007000	6.636984000	19.102008000
O	12.047003000	5.578994000	18.556995000
N	11.049987000	7.563043000	18.631003000
C	10.281009000	7.367970000	17.415982000
C	8.830001000	7.749012000	17.596026000
C	8.177550000	7.012196000	18.716823000
N	7.550142000	7.656106000	19.761637000
C	7.153753000	6.733429000	20.612060000
N	7.483907000	5.527147000	20.155916000
C	8.130771000	5.675768000	18.960646000
H	10.711686000	7.952254000	16.600884000
H	10.874977000	8.393359000	19.181629000
H	10.378298000	6.319597000	17.147194000
H	8.750778000	8.815439000	17.803582000
H	8.305478000	7.571491000	16.656419000
H	6.674465000	6.913535000	21.557818000
H	8.504125000	4.836222000	18.404956000
H	7.305567000	4.657894000	20.627844000
H	8.836099000	10.669282000	13.737748000
C	8.242008000	11.328014000	14.370985000
C	7.949987000	10.700975000	15.672015000
C	7.155381000	11.640406000	16.567410000
S	6.304887000	10.803435000	17.953915000
C	5.398882000	12.224015000	18.617798000
H	8.802650000	12.257785000	14.484364000
H	7.326499000	11.564413000	13.826651000
H	7.378130000	9.782421000	15.522162000
H	8.875500000	10.409422000	16.171110000
H	7.783887000	12.432999000	16.970292000
H	6.352789000	12.102997000	15.993192000
H	4.814718000	11.879438000	19.465403000
H	4.729664000	12.608553000	17.853095000
H	6.085185000	13.001894000	18.940831000

Fully optimized reduced site at BP86/def2TZVP level (Fig. 3D)

Cu	7.249441000	9.549508000	19.960915000
H	11.058216000	13.015447000	18.379055000
C	10.928025000	12.270015000	19.184989000
C	9.601958000	11.657991000	19.143028000
S	9.333020000	10.381754000	20.478702000
H	11.731408000	11.523492000	19.068608000
H	11.115112000	12.790737000	20.139127000
H	8.807961000	12.414759000	19.242586000
H	9.431560000	11.159129000	18.177340000
H	6.137972000	7.962001000	25.104210000
C	6.782999000	8.530995000	24.395017000
O	7.647995000	8.001000000	23.719980000
N	6.529977000	9.838987000	24.399015000
C	7.161025000	10.725055000	23.456040000
C	6.115069000	11.431942000	22.615837000
C	5.106838000	10.530949000	21.977832000
N	5.446803000	9.662505000	20.945927000
C	4.329461000	9.013452000	20.614675000
N	3.291593000	9.424558000	21.391951000
C	3.764969000	10.386082000	22.264591000
C	7.986957000	11.821992000	24.160052000
O	7.801023000	12.124995000	25.327016000
H	5.829660000	10.211508000	25.036636000
H	7.806779000	10.112851000	22.810740000
H	5.576902000	12.166651000	23.239131000
H	6.636121000	11.999344000	21.827381000
H	4.232987000	8.269250000	19.830900000
H	3.121766000	10.872238000	22.990031000
H	2.333807000	9.087830000	21.333588000
N	8.919995000	12.348008000	23.379983000
C	9.633998000	13.533001000	23.847998000
H	10.287583000	13.297685000	24.702207000
H	10.251742000	13.922114000	23.029231000
H	9.112178000	11.930001000	22.450971000

H	8.923627000	14.310490000	24.163932000
H	12.309375000	6.914393000	20.076277000
C	11.838988000	6.636973000	19.102035000
O	12.047015000	5.578985000	18.556979000
N	11.050008000	7.563144000	18.630968000
C	10.280984000	7.367799000	17.415944000
C	8.830003000	7.749152000	17.596156000
C	8.078355000	6.894461000	18.570594000
N	7.262782000	7.481657000	19.531268000
C	6.746477000	6.485328000	20.249603000
N	7.192655000	5.285677000	19.788873000
C	8.039894000	5.522942000	18.722348000
H	10.716835000	7.969941000	16.598917000
H	10.822020000	8.384856000	19.210749000
H	10.393823000	6.313913000	17.127307000
H	8.749787000	8.786823000	17.962028000
H	8.341433000	7.724094000	16.606999000
H	6.084445000	6.588088000	21.102902000
H	8.530776000	4.714433000	18.192084000
H	6.965216000	4.374817000	20.179363000
H	8.935166000	10.719940000	13.767714000
C	8.242048000	11.328027000	14.370970000
C	7.949904000	10.700985000	15.672050000
C	7.017463000	11.587533000	16.507681000
S	6.183968000	10.683447000	17.899890000
C	5.252384000	12.116617000	18.572249000
H	8.707018000	12.322096000	14.484558000
H	7.328333000	11.467380000	13.769868000
H	7.468686000	9.719305000	15.518913000
H	8.875466000	10.503846000	16.236073000
H	7.565416000	12.442698000	16.931885000
H	6.208204000	11.979359000	15.870972000
H	4.661595000	11.755096000	19.421195000
H	4.580277000	12.521622000	17.803724000
H	5.943741000	12.896834000	18.918025000

Fully optimized reduced site at B3LYP/def2TZVP level (Fig. 3E)

Cu	7.347343000	9.387033000	20.161025000
H	11.049037000	13.025937000	18.399005000
C	10.928038000	12.269971000	19.184978000
C	9.601909000	11.658036000	19.143068000
S	9.402905000	10.373689000	20.479912000
H	11.721957000	11.530736000	19.046385000
H	11.119304000	12.766413000	20.140669000
H	8.814607000	12.404299000	19.265953000
H	9.426651000	11.173121000	18.183674000
H	6.146895000	7.962211000	25.092709000
C	6.783001000	8.530984000	24.395020000
O	7.647992000	8.001010000	23.719983000
N	6.529979000	9.838979000	24.399005000
C	7.160996000	10.725053000	23.456082000
C	6.115144000	11.431910000	22.615680000
C	5.112810000	10.527692000	21.978200000
N	5.468003000	9.602130000	21.014439000
C	4.359772000	8.970366000	20.671915000
N	3.306178000	9.445457000	21.371237000
C	3.767225000	10.435706000	22.209601000
C	7.986952000	11.822002000	24.160083000
O	7.801033000	12.124997000	25.327031000
H	5.832317000	10.204157000	25.029304000
H	7.807163000	10.122004000	22.823903000
H	5.576173000	12.152278000	23.238407000
H	6.627263000	12.005504000	21.839936000
H	4.278174000	8.191362000	19.933276000
H	3.115212000	10.972506000	22.875968000
H	2.351646000	9.130681000	21.289074000
N	8.919983000	12.348011000	23.379991000
C	9.633997000	13.533002000	23.847993000
H	10.265963000	13.301843000	24.707507000
H	10.262174000	13.905220000	23.040903000
H	9.117125000	11.935799000	22.465531000

H	8.929296000	14.312192000	24.140176000
H	12.308365000	6.905589000	20.064803000
C	11.838995000	6.636988000	19.102036000
O	12.047003000	5.578987000	18.556987000
N	11.050025000	7.563158000	18.630937000
C	10.280962000	7.367717000	17.415920000
C	8.829999000	7.749241000	17.596262000
C	8.082454000	6.841948000	18.525990000
N	7.322719000	7.349051000	19.563716000
C	6.812141000	6.312289000	20.201986000
N	7.203355000	5.157560000	19.620464000
C	8.012252000	5.473822000	18.552305000
H	10.714130000	7.969848000	16.610119000
H	10.835819000	8.379751000	19.203042000
H	10.387936000	6.325246000	17.124725000
H	8.751367000	8.762777000	17.989800000
H	8.355142000	7.751612000	16.611249000
H	6.186514000	6.351505000	21.077266000
H	8.457182000	4.714948000	17.933403000
H	6.961101000	4.228211000	19.927588000
H	8.991769000	10.767453000	13.805580000
C	8.242016000	11.328016000	14.370964000
C	7.949918000	10.701010000	15.672100000
C	6.937311000	11.555237000	16.443964000
S	6.058830000	10.621597000	17.763248000
C	5.052248000	11.994228000	18.436054000
H	8.627138000	12.346276000	14.485320000
H	7.347803000	11.391042000	13.744614000
H	7.535160000	9.700462000	15.518213000
H	8.857386000	10.573104000	16.263940000
H	7.431034000	12.414775000	16.900934000
H	6.176247000	11.930105000	15.756243000
H	4.427268000	11.585108000	19.226020000
H	4.416962000	12.414814000	17.657104000
H	5.692354000	12.770692000	18.853526000

Fully optimized reduced site at B38HFP86/def2TZVP level (Fig. 3F)

Cu	7.332558000	9.487853000	20.040487000
H	11.059627000	13.004430000	18.384580000
C	10.928014000	12.270010000	19.184994000
C	9.601977000	11.657994000	19.143000000
S	9.378319000	10.420488000	20.482554000
H	11.717496000	11.524299000	19.076727000
H	11.104239000	12.785131000	20.131081000
H	8.818870000	12.411494000	19.234924000
H	9.436906000	11.158662000	18.189101000
H	6.150018000	7.962596000	25.089459000
C	6.783006000	8.531000000	24.395002000
O	7.647996000	8.000998000	23.719995000
N	6.529995000	9.839005000	24.399002000
C	7.160983000	10.725011000	23.456028000
C	6.115016000	11.431976000	22.615975000
C	5.134634000	10.524881000	21.969994000
N	5.496239000	9.646581000	20.979124000
C	4.405280000	9.008540000	20.630469000
N	3.357063000	9.430626000	21.351124000
C	3.801153000	10.396124000	22.211429000
C	7.986991000	11.821998000	24.160009000
O	7.801012000	12.124992000	25.327001000
H	5.830144000	10.201706000	25.021301000
H	7.806648000	10.122479000	22.822256000
H	5.569262000	12.141418000	23.241698000
H	6.630656000	12.011146000	21.848461000
H	4.334550000	8.255257000	19.865764000
H	3.146944000	10.896864000	22.901055000
H	2.413195000	9.098140000	21.266868000
N	8.920002000	12.348012000	23.379986000
C	9.634000000	13.532999000	23.848002000
H	10.269072000	13.296567000	24.700563000
H	10.254142000	13.907839000	23.039035000
H	9.104081000	11.940386000	22.464290000

H	8.927560000	14.305158000	24.146026000
H	12.307392000	6.902796000	20.061044000
C	11.838970000	6.636947000	19.102036000
O	12.047044000	5.578999000	18.556960000
N	11.049995000	7.563142000	18.631013000
C	10.281001000	7.367830000	17.415968000
C	8.830003000	7.749105000	17.596036000
C	8.101125000	6.886971000	18.564604000
N	7.302515000	7.440549000	19.533276000
C	6.814739000	6.443785000	20.230154000
N	7.256032000	5.271476000	19.753735000
C	8.078548000	5.530858000	18.692448000
H	10.713939000	7.964315000	16.610028000
H	10.833463000	8.372201000	19.203582000
H	10.386472000	6.323424000	17.134697000
H	8.756553000	8.776258000	17.956391000
H	8.346316000	7.719821000	16.617789000
H	6.166479000	6.528185000	21.084199000
H	8.567812000	4.746580000	18.145261000
H	7.038791000	4.365210000	20.127298000
H	8.913810000	10.715684000	13.768332000
C	8.242002000	11.328011000	14.370986000
C	7.949994000	10.700978000	15.672013000
C	7.050960000	11.595565000	16.510266000
S	6.233307000	10.705970000	17.873004000
C	5.356140000	12.110159000	18.599890000
H	8.717233000	12.304114000	14.489838000
H	7.331661000	11.480621000	13.788703000
H	7.453434000	9.739964000	15.516966000
H	8.869135000	10.486581000	16.218346000
H	7.619439000	12.425430000	16.930529000
H	6.260368000	12.011090000	15.884156000
H	4.779152000	11.739486000	19.441841000
H	4.683085000	12.552847000	17.868896000
H	6.061151000	12.859090000	18.954503000

Optimized inner-sphere ligands for oxidized, axial site at B38HFP86/def2TZVP level (Fig. 4A)

Cu	7.349299000	9.620275000	20.014537000
H	10.997606000	13.087789000	18.465061000
C	10.928027000	12.270003000	19.184981000
C	9.601973000	11.658023000	19.143016000
S	9.436988000	10.276347000	20.328699000
H	11.713411000	11.552762000	18.943762000
H	11.156764000	12.682297000	20.168895000
H	8.825705000	12.390209000	19.359272000
H	9.399388000	11.260569000	18.150479000
H	6.154072000	7.963589000	25.092297000
C	6.783015000	8.531001000	24.395007000
O	7.647999000	8.000995000	23.719997000
N	6.529995000	9.839001000	24.398995000
C	7.160955000	10.724987000	23.456041000
C	6.115024000	11.432039000	22.615991000
C	5.176315000	10.510357000	21.918221000
N	5.551920000	9.683102000	20.877474000
C	4.483551000	9.004053000	20.517590000
N	3.444634000	9.351162000	21.274173000
C	3.857781000	10.300158000	22.166628000
C	7.986990000	11.821971000	24.159996000
O	7.801006000	12.125000000	25.326989000
H	5.840303000	10.205576000	25.031050000
H	7.819541000	10.116345000	22.840643000
H	5.528272000	12.091658000	23.256803000
H	6.613542000	12.073914000	21.887338000
H	4.434798000	8.278140000	19.725762000
H	3.193875000	10.738436000	22.888122000
H	2.514850000	8.976720000	21.195065000
N	8.920011000	12.348024000	23.379993000
C	9.633998000	13.532996000	23.847999000
H	10.266254000	13.292913000	24.700780000
H	10.255204000	13.907969000	23.040449000
H	9.100024000	11.960204000	22.466285000

H	8.925862000	14.303442000	24.144657000
H	12.311701000	6.905013000	20.058111000
C	11.839004000	6.636988000	19.102020000
O	12.047008000	5.579000000	18.556989000
N	11.049971000	7.562977000	18.630999000
C	10.281020000	7.368067000	17.415998000
C	8.830003000	7.748942000	17.595965000
C	8.177097000	7.013150000	18.717019000
N	7.544089000	7.657037000	19.758491000
C	7.148315000	6.734529000	20.609212000
N	7.483512000	5.528315000	20.156412000
C	8.133745000	5.676990000	18.962917000
H	10.711613000	7.952689000	16.601071000
H	10.874914000	8.393202000	19.181691000
H	10.378599000	6.319827000	17.146937000
H	8.750645000	8.815520000	17.802492000
H	8.305513000	7.570803000	16.656364000
H	6.664820000	6.914536000	21.552805000
H	8.510997000	4.837576000	18.409632000
H	7.306295000	4.659324000	20.629282000
H	8.836322000	10.669354000	13.737877000
C	8.242017000	11.328004000	14.370986000
C	7.949975000	10.700999000	15.672015000
C	7.155059000	11.640946000	16.566910000
S	6.301546000	10.804984000	17.952514000
C	5.392973000	12.226224000	18.611825000
H	8.802437000	12.257883000	14.484380000
H	7.326525000	11.564131000	13.826499000
H	7.378115000	9.782451000	15.522264000
H	8.875412000	10.409668000	16.171345000
H	7.783760000	12.432899000	16.970630000
H	6.353634000	12.104255000	15.991672000
H	4.796121000	11.883032000	19.451339000
H	4.734411000	12.615377000	17.840152000
H	6.077989000	13.001009000	18.944926000

Optimized inner-sphere ligands for oxidized, rhombic site at B38HFP86/def2TZVP level (Fig. 4B)

Cu	7.353587000	9.617781000	20.015001000
H	10.998264000	13.087064000	18.464310000
C	10.928009000	12.270007000	19.184999000
C	9.601979000	11.658003000	19.142994000
S	9.439667000	10.276548000	20.329430000
H	11.713315000	11.552370000	18.944768000
H	11.156186000	12.683223000	20.168606000
H	8.825390000	12.389745000	19.359823000
H	9.399352000	11.260051000	18.150794000
H	6.154164000	7.963556000	25.092336000
C	6.783001000	8.530996000	24.395000000
O	7.648001000	8.000999000	23.719998000
N	6.529997000	9.839008000	24.399000000
C	7.160996000	10.725000000	23.456013000
C	6.115001000	11.431999000	22.615995000
C	5.177572000	10.509787000	21.917150000
N	5.555652000	9.678874000	20.880194000
C	4.487598000	8.999401000	20.519533000
N	3.446860000	9.350052000	21.271873000
C	3.858204000	10.301436000	22.162506000
C	7.987000000	11.821994000	24.160001000
O	7.801001000	12.124999000	25.327002000
H	5.839926000	10.205575000	25.030589000
H	7.819646000	10.116390000	22.840572000
H	5.527114000	12.089989000	23.257379000
H	6.613133000	12.075513000	21.888474000
H	4.440062000	8.271915000	19.729064000
H	3.192924000	10.741936000	22.881320000
H	2.516806000	8.976787000	21.190650000
N	8.920006000	12.348004000	23.379994000
C	9.633996000	13.533000000	23.848000000
H	10.264105000	13.293369000	24.702476000
H	10.257364000	13.906271000	23.041339000
H	9.099582000	11.960587000	22.466055000

H	8.926011000	14.304596000	24.142087000
H	12.311664000	6.905033000	20.058117000
C	11.839007000	6.636984000	19.102008000
O	12.047003000	5.578994000	18.556995000
N	11.049987000	7.563043000	18.631003000
C	10.281009000	7.367970000	17.415982000
C	8.830001000	7.749012000	17.596026000
C	8.177550000	7.012196000	18.716823000
N	7.550142000	7.656106000	19.761637000
C	7.153753000	6.733429000	20.612060000
N	7.483907000	5.527147000	20.155916000
C	8.130771000	5.675768000	18.960646000
H	10.711686000	7.952254000	16.600884000
H	10.874977000	8.393359000	19.181629000
H	10.378298000	6.319597000	17.147194000
H	8.750778000	8.815439000	17.803582000
H	8.305478000	7.571491000	16.656419000
H	6.674465000	6.913535000	21.557818000
H	8.504125000	4.836222000	18.404956000
H	7.305567000	4.657894000	20.627844000
H	8.836099000	10.669282000	13.737748000
C	8.242008000	11.328014000	14.370985000
C	7.949987000	10.700975000	15.672015000
C	7.155381000	11.640406000	16.567410000
S	6.304887000	10.803435000	17.953915000
C	5.398882000	12.224015000	18.617798000
H	8.802650000	12.257785000	14.484364000
H	7.326499000	11.564413000	13.826651000
H	7.378130000	9.782421000	15.522162000
H	8.875500000	10.409422000	16.171110000
H	7.783887000	12.432999000	16.970292000
H	6.352789000	12.102997000	15.993192000
H	4.814718000	11.879438000	19.465403000
H	4.729664000	12.608553000	17.853095000
H	6.085185000	13.001894000	18.940831000

Optimized inner-sphere ligands for reduced, axial site at B38HFP86/def2TZVP level (Fig. 6A)

Cu	7.646982000	9.136992000	20.347984000
H	11.055324000	13.024763000	18.401668000
C	10.928037000	12.270011000	19.184994000
C	9.601955000	11.657995000	19.143008000
S	9.509115000	10.416088000	20.512346000
H	11.714534000	11.526344000	19.051782000
H	11.111282000	12.761604000	20.141454000
H	8.807330000	12.392438000	19.270010000
H	9.419049000	11.150009000	18.198756000
H	6.150487000	7.962550000	25.089718000
C	6.783012000	8.531001000	24.395000000
O	7.647986000	8.000995000	23.719991000
N	6.530016000	9.838977000	24.398987000
C	7.160911000	10.725043000	23.456181000
C	6.115093000	11.431969000	22.615827000
C	5.221627000	10.481232000	21.903855000
N	5.705728000	9.510892000	21.058874000
C	4.661594000	8.854019000	20.615436000
N	3.528888000	9.348881000	21.133047000
C	3.865273000	10.384512000	21.960753000
C	7.986969000	11.821998000	24.160032000
O	7.801042000	12.124967000	25.326989000
H	5.828130000	10.201780000	25.019066000
H	7.807880000	10.125258000	22.820919000
H	5.509369000	12.083630000	23.248083000
H	6.626178000	12.068719000	21.892041000
H	4.685231000	8.029397000	19.925070000
H	3.130246000	10.949830000	22.503477000
H	2.600576000	9.015214000	20.944794000
N	8.919995000	12.348037000	23.379968000
C	9.634001000	13.532998000	23.848002000
H	10.271823000	13.296987000	24.698724000
H	10.251176000	13.910027000	23.037780000
H	9.119319000	11.931658000	22.471657000

H	8.926842000	14.303399000	24.148622000
H	12.308358000	6.903453000	20.060462000
C	11.838985000	6.636960000	19.102043000
O	12.047023000	5.578997000	18.556973000
N	11.049999000	7.563113000	18.630975000
C	10.280994000	7.367869000	17.415968000
C	8.830004000	7.749092000	17.596060000
C	8.105575000	6.804066000	18.493746000
N	7.567892000	7.210244000	19.689085000
C	7.050020000	6.146042000	20.254104000
N	7.225656000	5.069962000	19.476422000
C	7.895100000	5.464994000	18.352314000
H	10.716941000	7.967158000	16.612973000
H	10.844800000	8.380236000	19.197690000
H	10.382507000	6.324022000	17.133460000
H	8.746839000	8.751879000	18.016605000
H	8.358908000	7.770205000	16.612853000
H	6.562233000	6.114480000	21.212048000
H	8.159150000	4.773797000	17.573482000
H	6.929861000	4.134824000	19.691898000
H	8.993865000	10.771147000	13.810093000
C	8.242017000	11.328021000	14.370954000
C	7.949965000	10.700985000	15.672062000
C	6.930028000	11.523572000	16.441066000
S	6.232281000	10.607953000	17.844389000
C	5.208733000	11.925747000	18.539727000
H	8.619137000	12.346144000	14.489421000
H	7.348792000	11.385408000	13.746540000
H	7.553926000	9.694331000	15.518470000
H	8.857389000	10.588316000	16.265660000
H	7.389162000	12.438285000	16.818966000
H	6.111188000	11.807577000	15.778369000
H	4.730187000	11.537432000	19.434431000
H	4.445129000	12.236610000	17.829675000
H	5.825089000	12.779257000	18.814954000

Optimized inner-sphere ligands for reduced, rhombic site at B38HFP86/def2TZVP level (Fig. 6B)

Cu	7.379000000	9.640022000	20.043031000
H	11.076770000	12.984380000	18.368867000
C	10.928007000	12.270007000	19.184996000
C	9.601983000	11.658005000	19.142995000
S	9.412753000	10.466381000	20.523152000
H	11.716054000	11.519139000	19.107878000
H	11.090929000	12.807801000	20.120604000
H	8.814656000	12.408593000	19.215323000
H	9.444434000	11.128848000	18.204429000
H	6.150036000	7.962583000	25.089473000
C	6.783001000	8.530996000	24.394998000
O	7.648002000	8.000999000	23.720001000
N	6.530000000	9.839012000	24.399000000
C	7.160993000	10.724991000	23.456005000
C	6.114992000	11.432004000	22.616013000
C	5.142318000	10.526223000	21.959949000
N	5.520221000	9.684190000	20.946011000
C	4.444680000	9.027985000	20.584246000
N	3.389989000	9.405364000	21.320616000
C	3.813520000	10.359753000	22.203921000
C	7.987006000	11.821995000	24.159993000
O	7.800998000	12.125001000	25.327003000
H	5.831162000	10.201971000	25.022317000
H	7.806228000	10.122304000	22.821849000
H	5.566500000	12.137061000	23.244575000
H	6.631022000	12.016621000	21.852956000
H	4.390094000	8.292390000	19.801390000
H	3.149919000	10.826331000	22.908313000
H	2.454306000	9.051691000	21.231845000
N	8.920006000	12.348004000	23.379997000
C	9.633997000	13.532999000	23.848000000
H	10.264685000	13.298115000	24.704284000
H	10.258773000	13.903825000	23.040668000
H	9.106619000	11.940499000	22.463279000

H	8.928196000	14.308020000	24.140400000
H	12.307998000	6.903169000	20.060618000
C	11.839005000	6.636980000	19.102007000
O	12.047009000	5.578991000	18.556991000
N	11.049983000	7.563039000	18.631019000
C	10.281020000	7.367998000	17.415991000
C	8.829990000	7.748980000	17.595987000
C	8.121628000	6.934409000	18.619787000
N	7.358533000	7.537630000	19.586666000
C	6.900703000	6.578644000	20.352275000
N	7.324653000	5.381941000	19.920275000
C	8.106218000	5.586163000	18.816783000
H	10.714152000	7.961188000	16.607771000
H	10.839341000	8.373548000	19.202531000
H	10.384738000	6.322371000	17.138399000
H	8.754516000	8.791519000	17.907979000
H	8.334768000	7.671686000	16.626135000
H	6.290852000	6.709110000	21.228555000
H	8.576650000	4.774785000	18.293021000
H	7.124852000	4.496539000	20.349304000
H	8.902593000	10.709175000	13.762632000
C	8.241999000	11.328009000	14.370986000
C	7.950001000	10.700979000	15.672011000
C	7.067102000	11.606743000	16.515090000
S	6.256908000	10.734857000	17.893524000
C	5.363460000	12.144704000	18.589600000
H	8.730010000	12.297735000	14.489904000
H	7.330256000	11.493511000	13.794446000
H	7.441311000	9.746077000	15.519192000
H	8.870391000	10.476156000	16.212117000
H	7.645274000	12.436817000	16.921378000
H	6.271090000	12.021629000	15.895497000
H	4.789094000	11.785914000	19.438447000
H	4.687027000	12.563338000	17.847691000
H	6.059467000	12.908984000	18.928724000