Reduction of a platinum(IV) prodrug model by sulfur containing biological reductants: Computational mechanistic elucidation

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Table ESI1. Cartesian coordinates and total energies for all of the calculated structures in water

7 (L-Cys)

E(B3LYP/BS1) = -2150.640694 au
H(B3LYP/BS1) = -2150.503533 au
G(B3LYP/BS1) = -2150.556751 au
E(M06-2X/BS2//B3LYP/BS1) = -2150.718715 au

Pt	-0.11762800	0.00014300	-0.00003000
Cl	-1.75825500	0.16247200	1.72455700
Cl	-0.05045800	-2.38007100	0.21748000
Cl	-1.75847200	-0.16328200	-1.72428500
Cl	-0.05091000	2.38025400	-0.21753300
N	1.43606600	-0.13259300	-1.37579300
H	1.49025200	0.76004200	-1.87650600
N	1.43619200	0.13299400	1.37574900
H	1.49003300	-0.75941600	1.87695100
H	1.24051700	-0.86441200	-2.06461700
H	1.24094500	0.86522100	2.06421800
C	2.71039400	-0.41073800	-0.63822800
H	3.56059100	-0.15196300	-1.27359200
C	2.71066300	0.41021600	0.63808600
H	3.56071500	0.15088000	1.27342800
H	2.73419500	1.47942900	0.42111700
H	2.73320500	-1.47997200	-0.42124900

$TS_{7\text{-}9}$ (L-Cys)

E(B3LYP/BS1) = -2872.531032 au
H(B3LYP/BS1) = -2872.274536 au
G(B3LYP/BS1) = -2872.350759 au
E(M06-2X/BS2//B3LYP/BS1) = -2872.622475 au

N	3.08057400	-1.18406200	-1.61894700
H	2.98317700	-2.05803600	-1.07258600
C	4.15288000	-0.40338900	-0.90975400
C	4.18854400	1.07408700	-1.28267600
H	5.21507500	1.43200900	-1.17903300
H	3.86098000	1.24518700	-2.30955100
S	3.20868100	2.19268600	-0.16810700
H	2.16054400	-0.72355800	-1.60991700
H	3.32417800	-1.39478300	-2.59289500
Pt	-1.08696200	-0.27355600	0.22442800
Cl	-0.49682500	-1.54925300	-1.69184800
Cl	-4.79554400	-0.21534600	-1.21193600
Cl	-0.28265600	-1.93907900	1.71690600
Cl	1.02323500	0.97043600	0.07981700
N	-1.72028800	0.91704200	1.79704400
H	-0.91241700	1.40445800	2.19568500
N	-2.01329300	1.17368600	-0.91808300
H	-2.92944100	0.74340800	-1.19658500
H	-2.11866100	0.34301000	2.54493600
H	-1.47964000	1.40718400	-1.75886100

C -2.72917900 1.90243400 1.28597500
H -2.82506700 2.72918400 1.99355800
C -2.26597300 2.38252200 -0.07693500
H -3.02939500 3.00372100 -0.55317800
H -1.33738000 2.95327500 -0.00462700
H -3.68196400 1.37569900 1.20444600
C 4.03540300 -0.72683000 0.61227200
O 3.53212200 -1.84881800 0.88109300
O 4.47888400 0.15156600 1.38944900
H 5.09404100 -0.84108700 -1.25443800
H 2.69350200 2.95826500 -1.16031300

9 (L-Cys)
E(B3LYP/BS1) = -2872.531067 au
H(B3LYP/BS1) = -2872.273690 au
G(B3LYP/BS1) = -2872.353459 au
E(M06-2X/BS2//B3LYP/BS1) = -2872.622553 au
N -3.06990100 -1.14879200 1.66297700
H -3.02120700 -2.01887000 1.10247000
C -4.12723000 -0.31974400 0.98793400
C -4.07069900 1.16161100 1.34807000
H -5.08575400 1.56472300 1.33685100
H -3.64159800 1.32741300 2.33796700
S -3.15303700 2.23151100 0.13665800
H -2.13252700 -0.72421700 1.64082200
H -3.29978100 -1.36323000 2.63937200
Pt 1.07245100 -0.31718400 -0.25458500
Cl 0.48203300 -1.47201600 1.73982000
Cl 4.85329400 -0.03675400 1.41359400
Cl 0.20011700 -2.03600200 -1.64225900
Cl -1.01590400 0.97980300 -0.13460100
N 1.71067700 0.76816900 -1.89753100
H 0.91117800 1.26114400 -2.30646100
N 2.04089000 1.17199400 0.79637900
H 2.95000500 0.75406200 1.12147100
H 2.07642800 0.14457400 -2.62214800
H 1.50676900 1.47462800 1.61448100
C 2.75819100 1.74542200 -1.45368800
H 2.87618000 2.52561500 -2.20937100
C 2.32460300 2.31954200 -0.11782300
H 3.11272700 2.94191200 0.31457000
H 1.41479700 2.91600700 -0.21730500
H 3.69373400 1.19207700 -1.35014300
C -4.08476900 -0.66431000 -0.53375900
O -3.63067500 -1.80512700 -0.81030400
O -4.53195500 0.22037300 -1.30155400
H -5.07588100 -0.70567100 1.37079400
H -2.59106000 3.03381300 1.07397800

11 (L-Cys)
E(B3LYP/BS1) = -1690.608242 au
H(B3LYP/BS1) = -1690.475372 au0
G(B3LYP/BS1) = -1690.528658 au
E(M06-2X/BS2//B3LYP/BS1) = -1690.684857 au
Pt 0.51108400 0.03315200 -0.09577100
Cl 0.73903300 -2.27863900 -0.63464500
Cl 2.64709600 0.15669000 0.97535000
N 0.16494900 2.03710900 0.26078900
H 0.72872100 2.58837500 -0.39153500
N -1.36068500 0.11319500 -0.95099700
H -2.05327800 -0.33471100 -0.31072500
H 0.45486600 2.31206100 1.20134100
H -1.39312100 -0.39779200 -1.83529700
C -1.28714800 2.33261700 0.04740800
H -1.43907300 3.40611700 -0.09411900
C -1.74824900 1.54084200 -1.16264500
H -2.83145100 1.62090800 -1.29358100
H -1.25453800 1.89865100 -2.07006100
H -1.82163000 2.01103700 0.94412000
Cl -3.60215900 -1.05354200 1.00299200

10 (L-Cys)
E(B3LYP/BS1) = -1411.217542 au
H(B3LYP/BS1) = -1411.012300 au
G(B3LYP/BS1) = -1411.074255 au
E(M06-2X/BS2//B3LYP/BS1) = -1411.277507 au
N 2.77458400 1.02568400 -0.62344100
H 2.81101700 1.99050500 -0.25293200
C 1.37406000 0.83428000 -1.12827000
C 0.97417900 -0.62170400 -1.32568000
H 0.25693100 -0.70047700 -2.14108700
H 1.82198300 -1.28032900 -1.52202400
S 0.03326800 -1.35707600 0.11591000
H 3.00185000 0.38761200 0.15036800
H 3.47818900 0.90592900 -1.36068400
Cl 1.84822300 -1.37148200 1.49484600
C 0.42507300 1.67799500 -0.22597700
O 0.92188400 2.68484900 0.31627200
O -0.75616000 1.23336600 -0.17417800
H 1.35641400 1.29426000 -2.11998800
H 0.29524900 -2.65130700 -0.18368300
O -1.57511800 -1.64322300 -1.12389600
H -1.82661000 -2.59001800 -1.10005000
H -2.42135400 -1.11572600 -0.73854100
O -3.64541600 -0.48722500 -0.28244500
H -3.97343200 -0.00023400 -1.05924900
H -3.41884700 0.23086200 0.38230300

O -2.93007600 1.48983600 1.40459000
H -3.45331900 2.23722500 1.06733400
H -2.06304700 1.57607300 0.93220500

$TS_{7\text{-}8}$ (L-Cys)
E(B3LYP/BS1) = -2872.534409 au
H(B3LYP/BS1) = -2872.277481 au
G(B3LYP/BS1) = -2872.356219 au
E(M06-2X/BS2//B3LYP/BS1) = -2872.62093 au

Pt 0	-1.665244	0.244912	0.162569
Cl 0	-1.229978	2.087213	-1.281798
Cl 0	-1.452514	1.564274	2.140334
N 0	-2.091059	-1.450448	1.276852
N 0	-2.059982	-1.008082	-1.425817
C 0	-2.703787	-2.492376	0.389704
C 0	-2.015179	-2.427462	-0.962127
H 0	-1.221879	-1.801756	1.687385
H 0	-2.715223	-1.229683	2.056085
H 0	-3.030662	-0.751173	-1.682848
H 0	-1.441478	-0.855016	-2.224689
H 0	-2.595503	-3.479194	0.846456
H 0	-3.761977	-2.244616	0.290617
H 0	-2.518093	-3.072405	-1.688331
H 0	-0.967098	-2.726682	-0.889263
Cl 0	-5.033822	0.009914	-0.943007
Cl 0	0.856576	-0.473744	0.135638
N 0	5.916519	1.815186	-0.652490
C 0	5.235903	0.680433	0.049581
C 0	6.198041	-0.532651	0.019781
O 0	5.654392	-1.645019	0.278091
C 0	3.873957	0.394666	-0.576097
S 0	3.156382	-1.157973	0.100098
O 0	7.404765	-0.297243	-0.211171
H 0	5.704753	2.728004	-0.236264
H 0	5.681461	1.852033	-1.652237
H 0	6.931312	1.608072	-0.576865
H 0	5.115941	0.986561	1.092679
H 0	3.952724	0.222472	-1.653950
H 0	3.164509	1.201933	-0.385771
H 0	3.338478	-0.898448	1.414984

8 (L-Cys)
E(B3LYP/BS1) = -1181.935182 au
H(B3LYP/BS1) = -1181.811188 au
G(B3LYP/BS1) = -1181.856156 au
E(M06-2X/BS2//B3LYP/BS1) = -1181.953373 au

N 0	2.270957	-1.676973	0.104572
C 0	1.259150	-0.706690	-0.400051
C 0	1.722395	0.713662	-0.064994

O 0 2.897163 1.020726 0.029125
C 0 -0.122735 -0.945436 0.188768
S 0 -1.019969 0.680502 0.118110
O 0 0.709698 1.546558 0.073217
H 0 3.213900 -1.325612 -0.120612
H 0 2.154883 -2.602762 -0.326143
H 0 2.217278 -1.789373 1.126458
H 0 1.238169 -0.804595 -1.489532
H 0 -0.090878 -1.200993 1.252393
H 0 -0.710950 -1.677885 -0.359771
H 0 -1.071859 0.860397 -1.220188
Cl 0 -3.090322 -0.324465 -0.037968

$TS_{7\text{-}9}$ (L-Met)
E(B3LYP/BS1) = -2951.180698 au
H(B3LYP/BS1) = -2950.862773 au
G(B3LYP/BS1) = -2950.945155 au
E(M06-2X/BS2//B3LYP/BS1) = -2951.259700 au
Pt -1.34704200 -0.41093300 -0.22780800
Cl -0.63961300 0.53281600 -2.29541900
Cl -4.13170500 2.01967800 -0.00363500
Cl -1.88164200 -2.51729500 -1.21950700
Cl 1.05248500 -1.08409200 0.35807300
N -1.95823200 -1.07350000 1.63845200
H -1.23254200 -1.68508500 2.02208900
N -1.10857800 1.38156100 0.76458900
H -1.96632200 1.90455100 0.50222800
H -2.80941300 -1.63612400 1.56722200
H -0.26747500 1.91412400 0.49039600
C -2.17422300 0.10433200 2.54246400
H -2.13675000 -0.21986600 3.58528000
C -1.10315300 1.13546800 2.23666600
H -1.30197900 2.07095300 2.76797000
H -0.10882800 0.77943100 2.51543500
H -3.16403600 0.50495800 2.31616700
C 4.33538000 0.84125500 -0.55578600
C 4.16328900 -0.67810500 -0.55657300
C 2.32486800 2.01459900 0.63799200
C 3.03292000 1.62993800 -0.69069900
H 3.60717600 -1.02224400 -1.43385600
H 5.14700900 -1.15997300 -0.56093400
H 4.88692200 1.17263000 0.32852500
H 4.96726600 1.04237000 -1.42957200
H 2.30591500 1.08309900 -1.29883200
N 3.25613300 2.92106300 -1.43455100
H 3.42682400 2.77155100 -2.43497700
H 2.40679700 3.49069800 -1.30501000
H 4.05091700 3.44523400 -1.04879100
O 2.68623900 1.43321500 1.68455400

O 1.40836200 2.88476000 0.50910000
S 3.33066300 -1.40629700 0.91874600
C 3.50037600 -3.16465800 0.48958300
H 3.14462400 -3.34801600 -0.52657600
H 4.55797400 -3.43236400 0.57782200
H 2.91381700 -3.73586200 1.21225000

$TS_{7\text{-}8}$ (L-Met)
E(B3LYP/BS1) = -2951.175783 au
H(B3LYP/BS1) = -2950.857514 au
G(B3LYP/BS1) = -2950.943875 au
E(M06-2X/BS2//B3LYP/BS1) = -2951.255463 au
Pt -2.08224900 -0.24890600 0.05058800
Cl -1.81965900 -2.04920700 -1.49152800
Cl -5.31510100 0.11492200 -0.63673400
Cl -1.90983100 -1.67102100 1.96439600
Cl 0.52262100 0.26990400 0.01684900
N -2.32591200 1.42275800 1.25160900
H -1.42106800 1.66865100 1.66088300
N -2.39587800 1.10853100 -1.46991800
H -3.38654600 0.95062700 -1.71166600
H -2.95768400 1.22415100 2.03031400
H -1.81497000 0.93874200 -2.29306700
C -2.85272300 2.56053300 0.42913400
H -2.63592700 3.50993900 0.92522200
C -2.20919400 2.49448700 -0.94511700
H -2.66667800 3.21761000 -1.62631000
H -1.13607300 2.68991900 -0.89015800
H -3.93234600 2.42301700 0.35196100
C 4.86664100 -1.15671200 0.58101200
C 3.39430300 -0.95858200 0.22041900
C 6.28098900 0.75297200 -0.47061700
C 5.86257200 -0.73814300 -0.50352700
H 3.15278500 -1.44269800 -0.73064600
H 2.76014300 -1.38418000 1.00168200
H 5.10873600 -0.66788300 1.53021400
H 4.95727700 -2.23761900 0.74596900
H 5.45989600 -0.95536000 -1.49779100
N 7.13464600 -1.53561900 -0.39632500
H 7.08449600 -2.43546400 -0.88442200
H 7.87369000 -0.93301100 -0.80160200
H 7.38505400 -1.71422000 0.58343500
O 5.38293900 1.58322900 -0.16341800
O 7.47638900 1.00530400 -0.77270400
S 2.82687500 0.77934900 -0.00144800
C 2.92763800 1.44166800 1.68579700
H 2.52230800 0.71745400 2.39536700
H 3.97664100 1.65767400 1.89291500
H 2.34321500 2.36428800 1.70311600

8 (L-Met)
E(B3LYP/BS1) = -1260.576523 au
H(B3LYP/BS1) = -1260.391507 au
G(B3LYP/BS1) = -1260.442606 au
E(M06-2X/BS2//B3LYP/BS1) = -1260.581398 au
Cl -3.30317700 -0.40552000 -0.47835400
C 0.90439100 -1.31506700 0.66968700
C -0.51392300 -1.27605000 0.12169000
C 1.82441200 0.83892600 -0.30534100
C 1.91094700 -0.68569300 -0.28915600
H -0.59537800 -1.80368900 -0.83237800
H -1.21765700 -1.70734000 0.83406100
H 0.96526800 -0.83993500 1.65415200
H 1.13600900 -2.37874700 0.79892900
H 1.75786800 -1.05712100 -1.30783400
N 3.31524100 -1.05205500 0.08178200
H 3.51285700 -2.03574100 -0.13639300
H 3.97323100 -0.44872200 -0.42971000
H 3.48551000 -0.90615300 1.08537700
O 0.63859300 1.36397400 -0.16724000
O 2.84339400 1.51855800 -0.43013700
S -1.17112400 0.42169400 -0.25502400
C -1.52629600 1.09592400 1.40862600
H -1.97604500 0.31037100 2.01627400
H -0.58678800 1.44504500 1.83382600
H -2.22264900 1.92466000 1.26959700

9 (L-Met)
E(B3LYP/BS1) = -2951.181724 au
H(B3LYP/BS1) = -2950.862929 au
G(B3LYP/BS1) = -2950.948697 au
E(M06-2X/BS2//B3LYP/BS1) = -2951.262045 au
Pt 0 -1.418868 -0.556426 0.199732
Cl 0 -0.959688 0.214589 2.399573
Cl 0 -1.912331 -2.772179 0.944972
N 0 -1.878752 -1.056986 -1.755542
N 0 -1.177874 1.330737 -0.596054
C 0 -2.173220 0.199613 -2.516601
C 0 -1.166011 1.249422 -2.087164
H 0 -1.084654 -1.545828 -2.178078
H 0 -2.673104 -1.700021 -1.791726
H 0 -2.002392 1.897852 -0.296829
H 0 -0.306224 1.786927 -0.267922
H 0 -2.123681 0.003454 -3.590715
H 0 -3.186409 0.509084 -2.251611
H 0 -1.422460 2.226052 -2.507995
H 0 -0.153335 0.988790 -2.404596
Cl 0 -3.869169 2.950122 -0.043204

Cl 0 1.073222 -1.025785 -0.331681
C 0 4.683563 0.972295 0.156610
C 0 4.240977 -0.471194 0.420529
C 0 3.686633 2.104189 0.406792
S 0 3.291234 -1.260553 -0.951409
C 0 3.526148 -3.007486 -0.509276
N 0 3.283242 2.212166 1.853223
C 0 2.387942 2.086463 -0.441907
O 0 1.352361 2.521892 0.147133
O 0 2.502021 1.694104 -1.624441
H 0 5.037378 1.075159 -0.872468
H 0 5.557067 1.138775 0.798098
H 0 3.661791 -0.606056 1.339218
H 0 5.129838 -1.105953 0.498146
H 0 4.194460 3.046027 0.179770
H 0 3.281312 -3.169791 0.542454
H 0 4.572815 -3.259714 -0.705868
H 0 2.874178 -3.598893 -1.155324
H 0 2.381329 2.718499 1.855578
H 0 3.979506 2.705946 2.420812
H 0 3.112402 1.295847 2.281484

10 (L-Met)
E(B3LYP/BS1) = -1489.863434 au
H(B3LYP/BS1) = -1489.597251 au
G(B3LYP/BS1) = -1489.662528 au
E(M06-2X/BS2//B3LYP/BS1) = -1489.915891 au
Cl 0 0.132829 1.010984 -2.127286
C 0 1.323083 0.648859 1.714055
C 0 0.486567 1.611629 0.867805
C 0 2.287428 -0.329940 1.045004
S 0 -0.864018 0.869463 -0.193855
C 0 -1.876208 2.370319 -0.450501
N 0 3.427819 0.331576 0.318862
C 0 1.641297 -1.350009 0.071528
O 0 2.331732 -1.718055 -0.907073
O 0 0.483277 -1.728328 0.409162
H 0 0.675908 0.049101 2.356742
H 0 1.893298 1.303526 2.385173
H 0 1.075951 2.226116 0.183307
H 0 -0.066832 2.278208 1.533071
H 0 2.756140 -0.915825 1.840474
H 0 -1.222946 3.211404 -0.687766
H 0 -2.426868 2.542417 0.473448
H 0 -2.558091 2.158442 -1.276247
H 0 3.741212 -0.355645 -0.389319
H 0 4.201894 0.581409 0.942505
H 0 3.137207 1.177541 -0.184043

O 0 -2.070739 0.551756 1.721462
H 0 -1.497563 0.242830 2.447788
H 0 -2.570664 -0.280971 1.415736
O 0 -3.333429 -1.564205 0.795606
H 0 -2.710705 -2.002439 0.149358
H 0 -4.028060 -1.180505 0.233485
O 0 -1.606803 -2.733221 -0.964344
H 0 -1.684219 -2.182022 -1.761046
H 0 -0.749515 -2.441474 -0.555006

L-Cys
E(B3LYP/BS1) = -721.9385519 au
H(B3LYP/BS1) = -721.820116 au
G(B3LYP/BS1) = -721.862225 au
E(M06-2X/BS2//B3LYP/BS1) = -721.9582587 au
N 0.466753 -1.782174 0.143823
C 0.403747 -0.547958 -0.707496
C 1.304002 0.522637 -0.017814
O 2.140719 0.067071 0.812932
C -1.028549 -0.107550 -0.980427
S -2.002031 0.297388 0.533115
O 1.131020 1.710488 -0.377397
H 0.416568 -2.652898 -0.393881
H -0.287344 -1.780800 0.843781
H 1.368599 -1.703205 0.653047
H 0.873474 -0.806955 -1.661655
H -1.589549 -0.897911 -1.486587
H -0.999980 0.763887 -1.634899
H -1.265673 1.371636 0.893729

L-Met
E(B3LYP/BS1) = -800.5648914 au
H(B3LYP/BS1) = -800.384954 au
G(B3LYP/BS1) = -800.434864 au
E(M06-2X/BS2//B3LYP/BS1) = -800.5706575 au
C 0.03287300 0.05658800 0.97613500
C 1.35629400 0.82418100 0.87084700
C -2.19077400 -0.66413200 -0.11439000
C -0.94269700 0.26483800 -0.17755000
H 1.18394100 1.90203700 0.77340800
H 1.93582000 0.67467800 1.78781200
H 0.22256200 -1.01812100 1.03953400
H -0.45715700 0.34521400 1.91684300
H -0.44084900 0.08491800 -1.13224500
N -1.46498300 1.67984600 -0.22968700
H -1.02986900 2.24704900 -0.96236000
H -2.48547700 1.55307200 -0.41296200
H -1.35231400 2.16900900 0.66469100
O -1.96948600 -1.88413900 0.06731500

O -3.30987000 -0.09347900 -0.28250600
S 2.42433600 0.38249000 -0.55985300
C 2.91579900 -1.31927200 -0.10499700
H 3.39495300 -1.33326000 0.87867800
H 2.06225500 -2.00228600 -0.11090500
H 3.63750900 -1.65333800 -0.85578700

$TS_{2\text{-}12}$ (L-Met)
E(B3LYP/BS1) = -721.9219515 au
H(B3LYP/BS1) = -721.806429 au
G(B3LYP/BS1) = -721.847031 au
E(M06-2X/BS2//B3LYP/BS1) = -721.9386779 au
N 0.284760 -1.627811 0.797756
C 0.452075 -0.783307 -0.444074
C 1.302631 0.460302 -0.068203
O 2.519309 0.425212 -0.278381
C -0.929854 -0.470522 -1.021898
S -1.964643 0.501073 0.168577
O 0.676367 1.461551 0.470789
H -0.097955 -2.550434 0.556659
H -0.386761 -1.167879 1.433439
H 1.174832 -1.770767 1.289319
H 1.036679 -1.383627 -1.141263
H -1.437838 -1.404848 -1.279348
H -0.781123 0.093902 -1.947323
H -0.581377 1.228218 0.472784

12
E(B3LYP/BS1) = -721.9254434 au
H(B3LYP/BS1) = -721.805631 au
G(B3LYP/BS1) = -721.846313 au
E(M06-2X/BS2//B3LYP/BS1) = -721.9415261 au
N 0.105552 -1.589344 0.811111
C 0.426057 -0.799838 -0.431865
C 1.363361 0.364321 -0.059047
O 2.562963 0.301728 -0.279452
C -0.904740 -0.359315 -1.064191
S -1.982451 0.529546 0.151664
O 0.810536 1.429565 0.511505
H -0.252991 -2.518098 0.557411
H -0.660115 -1.073804 1.301032
H 0.911443 -1.718027 1.433281
H 0.987406 -1.459989 -1.092801
H -1.411745 -1.251534 -1.446891
H -0.667744 0.275800 -1.923844
H -0.221962 1.316964 0.541603

13
E(B3LYP/BS1) = -721.9213511 au

H(B3LYP/BS1) = -721.800705 au
G(B3LYP/BS1) = -721.84204 au
E(M06-2X/BS2//B3LYP/BS1) = -721.9378947 au
N -0.094821 -1.733664 -0.165532
C 0.256801 -0.439974 -0.831311
C 1.316411 0.316186 -0.044628
O 1.679429 1.434664 -0.354627
C -1.037630 0.389575 -0.954086
S -1.925276 0.459138 0.661203
O 1.832296 -0.382261 0.979703
H -0.526029 -2.379355 -0.835294
H -0.817794 -1.457413 0.559718
H 0.705772 -2.195683 0.275793
H 0.682328 -0.669893 -1.812812
H -1.657042 -0.067571 -1.735005
H -0.746795 1.382561 -1.307588
H 2.520439 0.162850 1.414205

$TS_{13\text{-}14}$
E(B3LYP/BS1) = au
H(B3LYP/BS1) = au
G(B3LYP/BS1) = au
E(M06-2X/BS2//B3LYP/BS1) = au
N 2.93548600 -1.25790500 -0.25153600
H 2.70115200 -0.92755700 0.69382100
C 4.00714100 -0.40396800 -0.85444700
C 3.57415200 1.06470900 -0.96583700
H 4.40043600 1.61591400 -1.42326700
H 2.72156600 1.13326600 -1.64785400
S 3.15416400 1.87632600 0.62242700
H 2.05835100 -1.24371100 -0.80538300
H 3.25267600 -2.23095500 -0.16726200
Pt -1.42114000 -0.17078000 0.06049100
Cl -0.18771600 -1.59285900 -1.45355300
Cl -3.93181400 -1.09819700 -0.74424000
Cl -1.12956700 -1.65146700 1.91967400
Cl 0.81007800 1.02122400 0.56649200
N -2.45048400 1.18158500 1.23604800
H -1.79320100 1.62881100 1.87986800
N -1.77172300 1.22735600 -1.42673800
H -2.54002200 0.84909900 -1.98929700
H -3.14765900 0.69246900 1.80147000
H -0.96097300 1.35450900 -2.03608300
C -3.11002400 2.20337600 0.36059900
H -3.33954200 3.09868200 0.94382500
C -2.17547900 2.52045400 -0.79244200
H -2.66427700 3.16283200 -1.52981800
H -1.26566400 3.01037100 -0.43971300

H -4.03716100 1.75853300 -0.00405500
C 5.26325000 -0.61127800 -0.01806000
O 5.32332000 -1.36696100 0.93348600
O 6.28287600 0.11862400 -0.47878800
H 7.06684300 -0.05483000 0.08210100
H 4.19632700 -0.79605200 -1.85870100

14

E(B3LYP/BS1) = -1181.971328 au
H(B3LYP/BS1) = -1181.845300 au
G(B3LYP/BS1) = -1181.891225 au
E(M06-2X/BS2//B3LYP/BS1) = -1181.996242 au
N 1.480305 -1.563637 0.762722
C 1.188689 -0.758651 -0.468524
C 1.439320 0.731686 -0.248406
O 1.296095 1.539271 -1.141758
C -0.202155 -1.066825 -1.038040
S -1.635368 -0.937463 0.086685
O 1.850835 1.008277 0.992017
Cl -1.878797 1.124280 0.308159
H 1.378772 -2.568623 0.566040
H 0.853054 -1.325840 1.542604
H 2.443773 -1.403591 1.083352
H 1.915336 -1.080997 -1.220012
H -0.240847 -2.120080 -1.345233
H -0.361630 -0.456459 -1.928978
H 2.024274 1.970056 1.065262

TS_A

E(B3LYP/BS1) = -2872.536378 au
H(B3LYP/BS1) = -2872.279933 au
G(B3LYP/BS1) = -2872.358752 au
E(M06-2X/BS2//B3LYP/BS1) = -2872.616094 au
N 5.90352300 -1.25080300 -1.03710100
H 6.77364900 -1.19239600 -1.57912500
C 5.05825300 -0.02463600 -1.20757500
H 5.03645700 0.18580100 -2.28127700
C 3.61391900 -0.40892500 -0.78903100
O 2.87148900 0.62849400 -0.61721000
C 5.65149800 1.18146800 -0.48765300
H 6.66018600 1.38724600 -0.85221800
H 5.02758800 2.04560400 -0.71756000
S 5.69256300 1.02927800 1.35234000
O 3.31983300 -1.60432900 -0.70815000
H 6.14503200 -1.40005100 -0.04819400
H 5.35813100 -2.07101300 -1.33636800
Pt -1.55941400 -0.20375900 0.28379600
Cl -1.56254700 -2.28022500 -0.86259000

Cl -5.11728300 0.32442300 -1.05637300
Cl -1.23017400 -1.23505400 2.40082900
Cl 0.80383700 0.17422500 -0.17985800
N -1.66370400 1.67374200 1.15415200
H -0.71312800 1.99583400 1.35966500
N -2.05195100 0.83350900 -1.42824000
H -3.07096900 0.63100500 -1.55323100
H -2.16419800 1.63381300 2.04606000
H -1.53271300 0.50770500 -2.24671500
C -2.34145200 2.61457500 0.20278600
H -2.11427800 3.64610700 0.48209000
C -1.85404400 2.29632500 -1.19933500
H -2.41640200 2.86231400 -1.94699400
H -0.79074000 2.51944500 -1.31058500
H -3.41568300 2.43922600 0.28612500
H 6.96053500 0.57556300 1.45668900

TS_B

E(B3LYP/BS1) = -2872.527779 au
H(B3LYP/BS1) = -2872.272299 au
G(B3LYP/BS1) = -2872.349615 au
E(M06-2X/BS2//B3LYP/BS1) = -2872.614719 au
N -3.07087500 -0.80417200 0.81427900
C -3.95100000 -0.50641200 -0.32759700
H -3.77083000 -1.28113300 -1.07473900
C -5.42675200 -0.69287500 0.10210400
O -5.98836900 0.25727400 0.86757800
C -3.63858600 0.84313600 -0.99128500
H -2.64986600 0.79648500 -1.45103900
H -4.36719700 1.01483200 -1.78754200
S -3.72407300 2.34187100 0.07903600
O -6.05909500 -1.67896400 -0.21583600
H -3.21024800 -0.19042500 1.62033200
H -3.15441400 -1.77708500 1.11497000
Pt 1.47784000 -0.38023800 -0.10968500
Cl 2.07911600 -1.71296800 1.75459600
Cl 4.63202600 1.59319300 0.48862700
Cl 1.55836300 -2.22912600 -1.60312800
Cl -0.93154300 -0.63610700 0.37678000
N 1.01072500 0.92818100 -1.65191200
H 0.01809500 0.83147700 -1.88447900
N 1.54916200 1.35400000 1.00520900
H 2.57394900 1.53577000 1.09556400
H 1.53673200 0.69474200 -2.49791400
H 1.13708500 1.24468400 1.93438200
C 1.31189400 2.33010500 -1.21120400
H 0.77476700 3.03914700 -1.84568600
C 0.90310200 2.46538500 0.24450900
H 1.22658100 3.42639000 0.65374900
H -0.17883900 2.37725200 0.36384100

H 2.38750400 2.47871700 -1.32359800
H -2.60546200 2.10832800 0.80189000
H -5.38492100 1.02604300 0.99811400

1

E(B3LYP/BS1) = -722.3903945 au
H(B3LYP/BS1) = -722.258298 au
G(B3LYP/BS1) = -722.300960 au
E(M06-2X/BS2//B3LYP/BS1) = -722.4017186 au
N -0.41696000 1.83589600 -0.16654600
H 0.10780800 2.60427500 0.27146700
C -0.35418800 0.60714000 0.69408500
H -0.79442800 0.89203600 1.65588500
C -1.22456800 -0.51067300 0.12558500
O -2.09644400 -0.06869700 -0.78568200
C 1.08907100 0.16665300 0.94124000
H 1.65239000 1.00180500 1.36614500
H 1.07858500 -0.63948700 1.67565300
S 2.01876800 -0.36967300 -0.55598100
O -1.13002900 -1.65998800 0.50429800
H -0.01585500 1.66968100 -1.09939800
H -1.38677300 2.14833800 -0.29708100
H 1.37017200 -1.54166200 -0.73061800
H -2.64357100 -0.82073300 -1.09492600

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E(B3LYP/BS1) = -722.3519701 au
H(B3LYP/BS1) = -722.218086 au
G(B3LYP/BS1) = -722.259008 au
E(M06-2X/BS2//B3LYP/BS1) = -722.3713725 au
N 2.02587800 0.46662700 -0.22329400
H 2.90160500 0.05830200 0.12753600
C 0.88015400 0.03554400 0.63666200
H 1.08793500 0.39587000 1.64455600
C -0.46339700 0.55496700 0.07501300
O -1.25951500 0.96615700 1.13734900
C 0.59623400 -1.46541600 0.50273400
H 1.38338400 -2.04264100 0.01369100
H 0.34125300 -1.92393300 1.45877400
S -0.89585400 -1.19341000 -0.57213300
O -0.28364900 1.52761200 -0.89630600
H 1.90799600 0.17158400 -1.20115700
H 2.12443600 1.48935400 -0.22014900
H -2.17647800 1.07818600 0.82403500
H -1.15024600 1.90072100 -1.14489900

TS_G

E(B3LYP/BS1) = -2872.970842 au
H(B3LYP/BS1) = -2872.697095 au

G(B3LYP/BS1) = -2872.775523 au
E(M06-2X/BS2//B3LYP/BS1) = -2873.056968 au
Pt -1.44888600 -0.20542700 0.05596500
Cl -1.16636900 -1.65829700 1.94056400
Cl 0.89542500 0.89068900 0.42476600
Cl -0.49685700 -1.76617500 -1.49229400
Cl -4.22663300 -0.83358200 -0.60357000
N -1.81344000 1.16011800 -1.45229700
H -2.66438500 0.81981200 -1.91232100
N -2.25624000 1.27843500 1.25651000
H -1.50813300 1.68789100 1.82133500
H -1.06113300 1.19036700 -2.14293100
H -2.94247300 0.88052800 1.90059800
C -2.04839000 2.50820000 -0.85065000
H -2.54835400 3.15927100 -1.57311300
C -2.89666000 2.32441100 0.39551000
H -2.98963400 3.26028100 0.95243400
H -3.88959800 1.95520300 0.13453800
H -1.07268100 2.93254900 -0.60553500
N 4.71509200 -0.78369100 -2.00715400
H 4.18317100 -0.53282700 -2.85214500
C 3.97686300 -0.27981100 -0.79518800
H 3.01619100 -0.79267600 -0.77187800
C 4.74785200 -0.67007500 0.45000800
O 4.13092600 -1.38805300 1.30536400
C 3.79347800 1.24139300 -0.88092900
H 4.76745600 1.72224800 -1.02571600
H 3.16510400 1.46243900 -1.74848200
S 3.07470200 1.92834000 0.65032900
O 5.96138200 -0.27659700 0.52207900
H 5.65062200 -0.36068300 -2.08599100
H 4.82110600 -1.80781800 -1.99703200
H 4.64175200 -1.62354100 2.11577700
H 6.45906500 -0.54953700 1.32756300

TS_m
E(B3LYP/BS1) = -2950.705695 au
H(B3LYP/BS1) = -2950.402805 au
G(B3LYP/BS1) = -2950.485393 au
E(M06-2X/BS2//B3LYP/BS1) = -2950.797747 au
Pt 1.40632800 0.38652400 -0.18546700
Cl 0.90975800 -0.34654700 -2.39305500
Cl 4.11228300 -2.09941300 -0.00219500
Cl 2.05992400 2.56615700 -0.92886500
Cl -1.04055300 1.01534100 0.31047300
N 1.86651100 0.86833200 1.77571200
H 1.10479800 1.42688300 2.17005600
N 1.03238900 -1.47523900 0.61814100
H 1.86079300 -2.02608700 0.33270900

H 2.70911200 1.44597100 1.82166900
H 0.14973400 -1.90242900 0.26446300
C 2.04436800 -0.39489300 2.56297200
H 1.96452000 -0.17951300 3.63167800
C 0.98545300 -1.38158100 2.10733100
H 1.16486200 -2.36921000 2.54307000
H -0.01859700 -1.05708200 2.38925000
H 3.04171600 -0.77561700 2.33556100
C -4.75301700 -0.83519500 -0.10142200
C -4.27538400 0.58714800 -0.40538800
C -3.79934300 -1.97080600 -0.50440400
H -3.69274900 0.63237800 -1.32929000
H -5.12746700 1.26867400 -0.50042100
H -5.02563000 -0.93886300 0.95277500
H -5.68074700 -0.95956600 -0.67485000
H -4.33420100 -2.90609800 -0.26100100
S -3.27688600 1.37040600 0.93220600
C -3.41165600 3.11323700 0.43270700
H -3.15220000 3.22468000 -0.62225100
H -4.44193900 3.43638200 0.60964900
H -2.72929500 3.69066700 1.05989300
N -3.46612000 -1.89173000 -1.93276800
H -2.64089800 -2.47287800 -2.06969000
H -4.22046000 -2.31286300 -2.47302900
C -2.51269000 -2.03993900 0.35227000
O -1.47986700 -2.51590400 -0.21887800
O -2.59446400 -1.68188900 1.55773000

3′

E(B3LYP/BS1) = -800.0830546 au
H(B3LYP/BS1) = -799.917523 au
G(B3LYP/BS1) = -799.967092 au
E(M06-2X/BS2//B3LYP/BS1) = -800.1038138 au
C 0.00505100 0.03879400 0.95163000
C -1.31740600 -0.73380700 0.92685700
C 2.25255600 0.56266200 -0.12740500
C 0.98390600 -0.32903600 -0.17218500
H -1.12930900 -1.81242400 0.90218500
H -1.89687900 -0.52588600 1.83341500
H -0.18468600 1.11603600 0.92050500
H 0.48637500 -0.17234400 1.91785200
H 0.49419600 -0.07699500 -1.12774600
N 1.34392500 -1.75653300 -0.11399200
H 0.72891100 -2.28133800 -0.73314400
H 2.28248600 -1.81906600 -0.50833400
O 2.07255500 1.80368400 0.04590500
O 3.37297800 -0.00180200 -0.30472500
S -2.41352100 -0.41328600 -0.51914900
C -2.92462900 1.30989800 -0.18462800
H -3.39116700 1.39142900 0.80218800

H -2.08121200 2.00250600 -0.25074200
H -3.66098700 1.58027300 -0.94691200

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E(B3LYP/BS1) = -1489.436603 au
H(B3LYP/BS1) = -1489.182170 au
G(B3LYP/BS1) = -1489.250485 au
E(M06-2X/BS2//B3LYP/BS1) = -1489.500604 au
Cl -1.89202100 -1.68457000 1.75953800
C -1.35968300 0.21793100 -1.91712500
C -0.88674600 -1.15496400 -1.42357700
C -1.74477000 1.28887700 -0.89357700
H -1.65950200 -1.71088400 -0.88932800
H -0.52108500 -1.74865700 -2.26587100
H -0.59631700 0.66113800 -2.56148700
H -2.22690800 0.01648200 -2.55602700
H -2.18744200 2.11755100 -1.45530700
S 0.50254300 -1.02957500 -0.23540100
C 1.13000700 -2.71654000 -0.22549500
H 0.38561800 -3.32440300 0.29331800
H 1.28018400 -3.05633600 -1.25233900
H 2.06861900 -2.70736200 0.33406900
N -2.81037000 0.83766800 0.06340500
H -2.93256000 1.58920800 0.75506600
H -3.70020600 0.66180300 -0.41441800
H -2.53782200 -0.02545400 0.60521200
C -0.60873500 1.93231000 -0.04810100
O -0.94803600 2.43848900 1.03874900
O 0.56220200 1.95100100 -0.56130000
O 1.64903000 -0.34134700 -1.21535800
H 1.41902000 0.64306000 -1.13119500
H 3.46670000 -0.24581500 -0.38898700
O 4.17747100 -0.05616500 0.25343400
H 3.11322300 1.21112100 1.12576600
H 4.09426200 -0.78052100 0.89690600
O 2.47483300 1.82485700 1.55001600
H 1.82605100 2.00592600 0.83797200

17

E(B3LYP/BS1) = -1488.988656 au
H(B3LYP/BS1) = -1488.746617 au
G(B3LYP/BS1) = -1488.815769 au
E(M06-2X/BS2//B3LYP/BS1) = -1489.063050 au
Cl -3.03034700 -1.16885800 1.41932900
C -0.80161300 0.35537100 -2.00146600
C -0.65614000 -1.02312700 -1.35004900
C -1.26511800 1.51720000 -1.11382500
H -1.54349800 -1.31690500 -0.77880900
H -0.46772800 -1.77726800 -2.12177000
H 0.14846100 0.65928500 -2.45027200

H -1.51505500 0.24245700 -2.82670500
H -1.38268000 2.39485900 -1.75583900
S 0.75386500 -1.16502900 -0.18091400
C 0.42586400 -2.87566500 0.33133500
H -0.51564400 -2.88746700 0.88907100
H 0.37085700 -3.52634800 -0.54635800
H 1.24888000 -3.18458600 0.98112100
N -2.62331000 1.26514000 -0.52045500
H -2.88134500 2.06544700 0.06551200
H -3.33227100 1.15187600 -1.25267300
H -2.66509500 0.42106700 0.11508000
C -0.28658400 1.91283100 0.01917000
O -0.75200700 2.01284000 1.17968300
O 0.90074500 2.12846100 -0.36417900
O 2.02310400 -1.21166600 -1.07143100
H 3.42315900 -0.59415600 -0.23539300
O 4.20787000 -0.25862700 0.27216100
H 3.28393500 1.01862200 1.22571500
H 4.32000000 -0.91982800 0.97531300
O 2.71742200 1.66294400 1.70698100
H 2.04973200 1.91677100 1.02851800

18

E(B3LYP/BS1) = -1181.519904 au
H(B3LYP/BS1) = -1181.407787 au
G(B3LYP/BS1) = -1181.453571 au
E(M06-2X/BS2//B3LYP/BS1) = -1181.552361 au
N -1.35601500 1.49569000 -0.87860200
H -1.85941700 2.38312900 -0.78635200
C -1.18078300 0.77344400 0.42465800
H -1.93497600 1.17194100 1.10875900
C -1.54925000 -0.72613600 0.18019100
O -1.35744500 -1.49995100 1.14360000
C 0.18010400 1.01531200 1.07584500
H 0.26551500 2.05359400 1.42533700
H 0.27256600 0.36145100 1.94459600
S 1.66910500 0.88531200 0.02422500
O -2.05454900 -0.97851700 -0.95113800
H -0.45912900 1.67683300 -1.34784500
H -1.89232800 0.81684900 -1.46271100
Cl 1.82292500 -1.15568200 -0.39664900

19

E(B3LYP/BS1) = -1410.821836 au
H(B3LYP/BS1) = -1410.625332 au
G(B3LYP/BS1) = -1410.687233 au
E(M06-2X/BS2//B3LYP/BS1) = -1410.890983 au
N 1.57660900 2.08442100 0.16492200
H 1.65858100 3.04324900 0.51918400

C 0.41700900 1.36817000 0.80588900
H 0.19617200 1.87433300 1.74742700
C -0.79205400 1.53000200 -0.15460200
O -1.92286100 1.26840500 0.34561900
C 0.74088200 -0.09161100 1.13789800
H 1.52622900 -0.15276500 1.89557400
H -0.15574200 -0.54921400 1.55991000
S 1.23521100 -1.18586300 -0.26184700
O -0.53663900 1.89551600 -1.32700500
H 2.48191400 1.61898700 0.29230200
H 1.33722100 2.14165900 -0.84454300
O -1.24416300 -1.87853300 -0.52396100
H -1.13796700 -2.84414000 -0.57493300
H -1.74235500 -1.72490600 0.31989900
O -2.91413100 -1.04135500 1.51705700
H -3.53739900 -0.98427600 0.76035900
H -2.46243800 -0.17153700 1.43116800
O -3.65141400 -0.34540000 -1.15559500
H -2.93906600 -1.00091600 -1.29363400
H -3.14292100 0.41028600 -0.77987900
Cl 3.35745700 -0.78272600 -0.21069200

TS_n

E(B3LYP/BS1) = -1410.815194 au
H(B3LYP/BS1) = -1410.623358 au
G(B3LYP/BS1) = -1410.681904 au
E(M06-2X/BS2//B3LYP/BS1) = -1410.87267 au
N 1.38444200 2.02801400 0.21050800
H 1.67834500 2.86062800 0.72913800
C 0.34262100 1.24152900 0.95975500
H 0.22342200 1.70838900 1.93979800
C -0.98973500 1.40507100 0.18319100
O -2.04164400 1.07845600 0.81179700
C 0.77174200 -0.21190300 1.22268200
H 1.67497200 -0.22366500 1.83584500
H -0.02361000 -0.69586000 1.79399600
S 1.09627000 -1.31284800 -0.23258900
O -0.92002700 1.86433300 -0.98103300
H 2.22471900 1.45888000 -0.02759000
H 0.92178900 2.32188300 -0.67094600
O -0.48889800 -2.39066500 -0.05552400
H -0.29864400 -3.04662000 0.64308300
H -1.48868100 -1.93988200 0.20281900
O -2.66897400 -1.50303500 0.59164400
H -3.14705100 -1.15976600 -0.21471100
H -2.41429500 -0.64137700 1.01342000
O -3.74789500 0.17795000 -1.23401600
H -3.14279000 0.16356000 -1.99549000
H -3.27172500 0.75579800 -0.58997800
Cl 3.41316900 -0.18688200 -0.56871900

20

E(B3LYP/BS1) = -1257.509769 au
H(B3LYP/BS1) = -1257.381804 au
G(B3LYP/BS1) = -1257.432026 au
E(M06-2X/BS2//B3LYP/BS1) = -1257.557099 au
N -0.62885000 -1.22125000 -0.66335300
H -0.65488800 -2.21741700 -0.90387800
C 0.29440200 -0.98974300 0.49510000
H 0.09909400 -1.77027000 1.23174600
C 1.75716600 -1.09864100 -0.01277300
O 2.60092300 -1.55032700 0.78878200
C 0.01056700 0.37621600 1.13668400
H -1.01486700 0.40399300 1.52325100
H 0.70016600 0.52643900 1.97244300
S 0.10781700 1.80823000 0.00416100
O 1.95800200 -0.66511400 -1.19465500
H -1.62103700 -0.89340800 -0.47461200
H -0.23721800 -0.72345100 -1.47396300
O 1.77656400 1.92622900 -0.27613000
H 1.99372200 1.14555200 -0.84365000
Cl -3.50851800 -0.25103800 -0.04191100

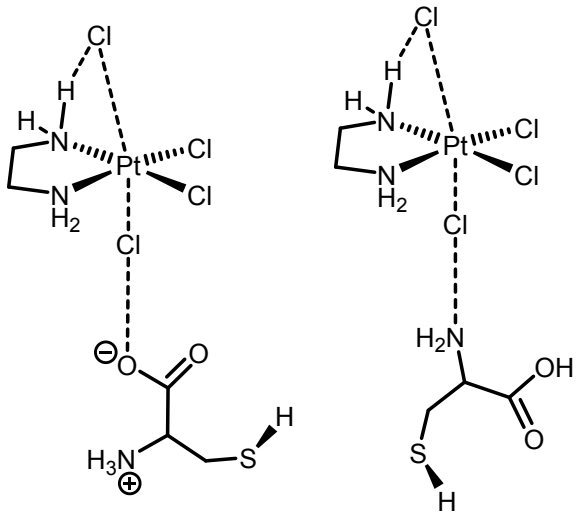
$(H_2O)_3$
E(B3LYP/BS1) = -229.2858809 au
H(B3LYP/BS1) = -229.205263 au
G(B3LYP/BS1) = -229.241976 au
E(M06-2X/BS2//B3LYP/BS1) = -229.3290001 au
H 0.65927500 -0.93888800 0.05268100
O 1.53597700 -0.48992700 0.12460000
H 0.49464400 1.04224000 -0.00168200
H 1.88860500 -0.53729200 -0.77986100
O -0.33177000 1.57314000 -0.10500200
H -0.54763800 1.83065900 0.80696400
H -1.13886700 -0.10251100 -0.15374600
O -1.19361300 -1.08761300 -0.11170900
H -1.44077200 -1.25901200 0.81253400

$(H_2O)_2$
E(B3LYP/BS1) = -152.8496826 au
H(B3LYP/BS1) = -152.797589 au
G(B3LYP/BS1) = -152.829834 au
E(M06-2X/BS2//B3LYP/BS1) = -152.8833881 au
O -1.45296300 0.10228900 0.05753800
H -1.76024700 -0.70604800 -0.38227000
H -0.47266900 0.02996500 -0.00171400
O 1.34510300 -0.09884800 -0.08381700
H 1.56782600 0.82865200 -0.27380200
H 1.52797700 -0.18009700 0.86801700

TS_P

E(B3LYP/BS1) = -1903.452429 au
H(B3LYP/BS1) = -1903.218354 au
G(B3LYP/BS1) = -1903.286437 au
E(M06-2X/BS2//B3LYP/BS1) = -1903.506216 au

N 1.21318300 -1.42513600 -0.97529300
H 0.16395900 -1.23816900 -1.07446400
C 1.74666400 -1.11130800 0.38620100
H 1.18836300 -1.73840000 1.08753900
C 3.24531200 -1.52034000 0.47883800
O 3.76788900 -1.36172400 1.61101200
C 1.46862800 0.34087300 0.77816000
H 0.39017000 0.52050700 0.88293500
H 1.93190100 0.54429400 1.74574900
S 1.93981300 1.64267100 -0.42024800
O 3.76558900 -1.98453600 -0.56934900
H 1.71545300 -0.88102700 -1.68550400
H 1.40310200 -2.40916600 -1.18953100
Cl 4.01178300 1.80742100 -0.18052400
N -2.55239800 1.45462000 0.55003700
H -1.74788400 1.61903100 1.16638200
C -3.24712600 0.18319700 0.92935400
H -3.37693200 0.18845500 2.01551200
C -4.63573500 0.10800600 0.31035200
O -5.33927800 -0.87728500 0.41658800
C -2.37038600 -0.99928400 0.48337600
H -1.47935200 -1.02226800 1.12115000
H -2.93854300 -1.91196800 0.67904600
S -1.91300500 -0.85522100 -1.30068300
O -5.00409400 1.23530800 -0.31607300
H -2.18934500 1.30115300 -0.41939500
H -3.16643100 2.27499500 0.57557000
H -5.91417400 1.11983000 -0.65951200



TS$_A$ **TS$_B$**

47.2 48.4

Scheme ESI1 Transition structures **TS$_A$** and **TS$_B$** showing reduction of [$PtCl_4$(en)] by carboxylate and amine functional groups of L-Cys. The relative Gibbs free energies are shown in kcal/mol.

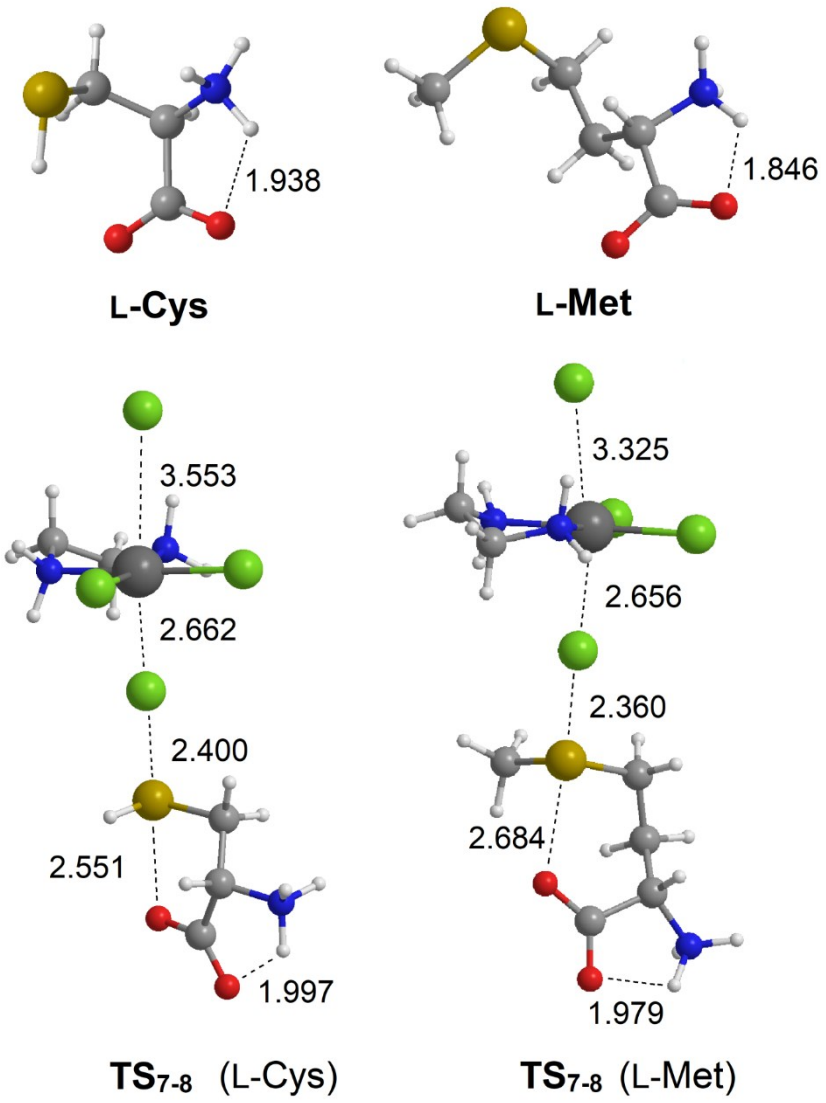


Fig. ESI1 Selected bond distances (Å) calculated for L-Cys, L-Met, **TS$_{7\text{-}8}$** for L-Cys, and **TS$_{7\text{-}8}$** for L-Met.

Computational details

Gaussian 09 [S1] was used to fully optimize all the structures reported in this paper at the B3LYP level of theory. [S2] For all the calculations, solvent effects were considered using the SMD solvation model with water as the solvent. [S3] The effective-core potential of Hay and Wadt with a double-ξ valence basis set (LANL2DZ) was chosen to describe Pt. [S4] The 6-31G(d) basis set was used for other atoms.[S5] A polarization function was also added for Pt ($\xi_f = 0.993$). [S6] This basis set combination will be referred to as BS1. Frequency calculations were carried out at the same level of theory as those for the structural optimization. Transition structures were located

using the Berny algorithm. Intrinsic reaction coordinate (IRC) calculations were used to confirm the connectivity between transition structures and minima.[S7] To further refine the energies obtained from the B3LYP-SMD/BS1 calculations and to consider dispersive interactions,[S8] we carried out single-point energy calculations using the M06-2X functional method[9] for all of the structures with a larger basis set (BS2) and the SMD solvation model. BS2 utilizes the def2-TZVP basis set [S10] on all atoms. Effective core potentials including scalar relativistic effects were used for the platinum atom. Tight convergence criterion was also employed to increase the accuracy of the calculations. We used the results obtained from the M06-2X-SMD/BS2//B3LYP-SMD/BS1 calculations for interpreting our findings.

Given that the solvation free energy and gas phase free energy of a proton are reported as -264.0 and -6.3 kcal/mol, respectively, a number of -270.3 kcal/mol was used as the free energy of H^+ in the calculations. [S11]

In this work, the free energy for each species in solution was calculated using the following formula:

$$G = E(BS2) + G(BS1) - E(BS1) + \Delta G^{1atm \rightarrow 1M} \quad (1)$$

where $\Delta G^{1atm \rightarrow 1M} = 1.89$ kcal/mol is the free-energy change for compression of 1 mol of an ideal gas from 1 atm to the 1 M solution phase standard state. [S12]

An additional correction to Gibbs free energies was made to consider solvent (water) concentration where a water cluster $(H_2O)_n$ is directly involved in transformations. In such a case, the free energy of $(H_2O)_n$ is described as follows:

$$G = E(BS2) + G(BS1) - E(BS1) + \Delta G^{1atm \rightarrow 1M} + RT \ln(55.34/n) \quad (2)$$

where the last term corresponds to the free energy required to change the standard state of $(H_2O)_n$ from 55.34/n M to 1 M.[S13]

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