On pH controlling of the reaction mechanism: Interactions of Au(I)-NHC Complex with Thioredoxin Reductase (modeled by Cysteine and Selenocysteine); ab initio and DFT calculations.

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Supplementary material

S. 1 Comparison of calculated and experimental pKa values

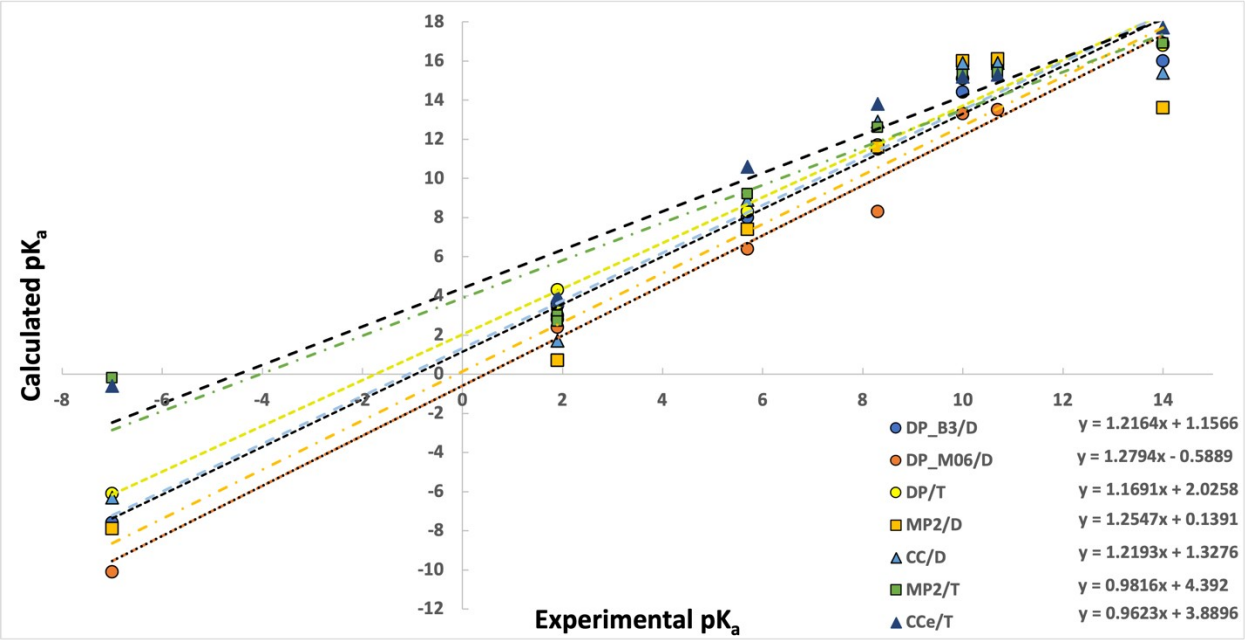


Figure S1: Comparison of calculated and experimental[1,2] pK_a values based on the results presented in Table 1 i.e., for proton dissociations in HCl, carboxyl , selenol/thiol, and amino groups of Cys and Sec amino acids, respectively, together with ionic product of water. Compared methods include DFT calculations with the B3LYP, and M06-2X functionals and double-ζ basis set and in the case of the B3LYP functional also triple-ζ basis set (all of them include Grimme's dispersion corrections). The post-HF calculations (MP2 and CC) employ both double-ζ and triple-ζ basis sets. Detailed descriptions of models can be found in the *Computational details* section in the main text.

The root mean square deviations (RMSD) in Table 1 (main text) are calculated according to formula

$$RMSD = \sqrt{\frac{\sum_{i=1}^{N} (pK_{acalc,i} - pK_{aexp,i})^2}{N}}$$

where $pK_{aexp,i}$ are available experimental pK_a values and $pK_{acalc,i}$ corresponding calculated value, in our case N=7.

S.2 Wertz's reduction of entropy coming from translational and rotational degrees of freedom

There is a generally accepted fact that the entropy of molecules is reduced during their transfer from the gas phase to the liquid phase due to restriction of their free volume. Based on experimental data, Wertz [3] noticed that change of the entropy is rather same for small molecules while the enthalpies associated with solvation differ significantly. Within his explanation, the change of entropy of solvent (configuration and mixing) was assumed to be negligible while the dominant contribution follows from the reduction of translational and rotational degrees of freedom of a molecule. In the case of vibrational degrees of freedom, the situation is more complicated as the degree of reduction of pertinent entropy contribution depends on the amplitude of a given vibrational mode. For transfer of molecules to water, it was suggested based on measured entropies that the entropy of a molecule in aqueous solution is reduced to 54 % of its original gas phase entropy when standard states of 55.5 mol·dm^{-3} are considered for both gas and aqueous states. This entropy loss of 46 % describes sufficiently solvation of alcohols and alkanes, but not secondary and tertiary amines. Although this reduction factor is not constant or in a narrow range for all molecules, this simple approach leads to a better estimation of the entropy changes during solvation.

In calculations, standard states of 55.5 mol·dm^{-3} concentration are not typically considered. When we start from the standard state of 1 atm for gas phase and end with solution of 1 mol·dm^{-3} concentration, two other contribution to the change of entropy must be included: a) initial entropy decrease of 14.3 cal·K^{-1}·mol^{-1} associated with the compression of the ideal gas to 55.5 mol·dm^{-3} concentration, and b) final entropy increase of 8.0 cal·K^{-1}·mol^{-1} given by dilution of the solution to 1 mol·dm^{-3} concentration. Altogether, the change of the entropy ΔS_{solv} in the process of solvation can be evaluated as

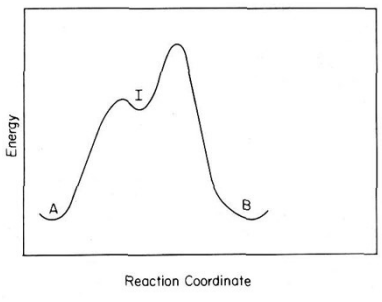
$$\Delta S_{solv} = -0.46 \cdot \left(S_{gas}^{trans} + S_{gas}^{rot} - 14.3 \right) + 8.0$$

when only entropy given by translational and rotational degrees of freedom is reduced since scaling of the vibrational part is complicated. In addition, Abraham [4] suggested to use more general expression for different compounds and solvents in the form

$$\Delta S_{solv} = m\, S_{gas} + c$$

where the *m* and *c* constants must be fitted for given combination of solvent and a type of compounds.

S.3 Derivation of eq 6 - Estimation of rate limiting step[5]



Let's assume a two-step process:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} B$$

where the first step is rate limiting and the following inequalities are valid: $k_1 \ll k_{-1}$, $k_{-2} \ll k_2$ and $k_1 \ll k_2$. Thus, concentration of an intermediate [I] is low and a steady

state condition can be applied: $d[I]/dt \cong -k_1.I - k_2.I + k_1.A = 0$

Then $d[B]/dt = k_2.I$ (reverse process is neglected). Substituting $.I$ from above final reaction is immediately obtained:

$$\frac{d[B]}{dt} = \frac{k_2.k_1}{(k_2 + .k_{-1})}A$$

References:

(1) Huber, R. E.; Criddle, R. S. Comparison of the chemical properties of selenocysteine and selenocystine with their sulfur analogs. *Arch Biochem Biophys* **1967**, *122* (1), 164-173. DOI: 10.1016/0003-9861(67)90136-1 From NLM.
(2) Lide, D. R. CRC Handbook of Chemistry and Physics; 7-1 Properties of Amino Acids. 88th ed.; CRC Press: 2007; Vol. 7-1 Properties of Amino Acids, p 2640.
(3) Wertz, D. H. Relationship between the Gas-Phase Entropies of Molecules and Their Entropies of Solvation in Water and 1-Octanol. . *J. Am.chem. Soc.* **1980**, *102*, 5316-5322.
(4) Abraham, M. H. Relationship between solution entropies and gas phase entropies of nonelectrolytes. *Journal of the American Chemical Society* **1981**, *103* (22), 6742-6744. DOI: 10.1021/ja00412a036.
(5) Murdoch, J. R. What is the rate-limiting step of a multistep reaction? *Journal of Chemical Education* **1981**, *58* (1), 32. DOI: 10.1021/ed058p32.

S. 4 XYZ coordinates of stationary points on the reaction coordinates

Cys

Deprotonated branch

Reactant:

24

-710.549620

Au	-0.806816	-0.984248	-0.043980
Cl	0.686185	-2.762865	-0.461165
C	-2.040032	0.545153	0.278266
C	-3.757087	1.836867	0.963543
H	-1.036606	2.089047	-0.734247
H	-4.686390	2.061655	1.463107
H	-2.954294	3.664492	-0.020844
C	-2.908239	2.617761	0.236857
N	-1.874435	1.802979	-0.169170
N	-3.199939	0.574150	0.971340
N	2.608904	-0.019180	-1.118872
H	2.199706	-0.806160	-0.593593
C	2.929482	1.103932	-0.201410
H	3.705549	1.702554	-0.683128
C	1.666084	1.954659	-0.011457
H	0.957966	1.408173	0.624091
H	1.959584	2.861737	0.520691
C	3.438223	0.557836	1.147529
O	3.200525	-0.654309	1.396645
O	4.012758	1.395353	1.889482
H	3.429371	-0.369725	-1.612516
H	1.917932	0.348411	-1.806982
S	0.859924	2.366483	-1.614422
H	-3.596874	-0.230841	1.436291

TS:

24

-710.533843

Au	-0.581411	-0.892177	0.011212
Cl	-0.030582	-3.269580	0.477573
C	-1.792739	0.706314	-0.040250
C	-3.585257	2.039057	-0.413631
H	-0.653604	2.212353	0.864540
H	-4.572185	2.290401	-0.769429
H	-2.644374	3.810230	0.547938
C	-2.641503	2.778479	0.232220
N	-1.566547	1.941992	0.449267
N	-3.040534	0.778871	-0.565047
N	3.032581	0.717421	1.311290
H	2.671446	-0.228576	1.026122
C	2.922056	1.554287	0.089437
H	3.741357	2.280123	0.099708
C	3.026034	0.665048	-1.157917
H	2.635713	1.241400	-1.998693
H	4.080208	0.447883	-1.356344
C	1.606631	2.353925	0.172822
O	0.996630	2.317537	1.289058
O	1.267608	2.994793	-0.842971
H	2.403442	1.115097	2.021420
H	3.982450	0.632377	1.670634
H	-3.507045	-0.002623	-1.003134
S	2.125640	-0.930192	-0.958787

Deprotonated branch

Reactant:

24

-709.701692

Au	-1.009650	-1.058115	-0.148506
Cl	0.378718	-2.837845	-0.832284
C	-2.149812	0.472545	0.421379
C	-3.795197	1.741739	1.299889
H	-1.013241	2.096877	-0.253736
H	-4.724352	1.938729	1.811245
H	-2.828012	3.655565	0.702016
C	-2.866999	2.578814	0.756670
N	-1.879525	1.776721	0.228042
N	-3.329670	0.461256	1.079490
N	2.667144	-0.364476	-0.909369
H	2.118881	-1.176423	-0.587596
C	2.982225	0.540701	0.227949
H	3.828020	1.159299	-0.080427
C	1.768748	1.425905	0.512125
H	0.957488	0.818942	0.929121
H	2.059291	2.168603	1.255615
C	3.365018	-0.292298	1.470778
O	3.047051	-1.511067	1.460047
O	3.932508	0.345207	2.394416
H	3.505620	-0.721030	-1.367653
H	2.106130	0.180020	-1.593759
H	-3.802343	-0.383598	1.370617
Se	1.095608	2.338395	-1.119419

TS:

24

-709.687517

Au	-0.704554	-0.915445	0.061997
Cl	0.056363	-3.239109	0.551588
C	-2.082858	0.539703	-0.065640
C	-4.013168	1.643333	-0.495823
H	-1.120828	2.216514	0.754447
H	-5.022171	1.764761	-0.857660
H	-3.274911	3.555179	0.368907
C	-3.157208	2.515379	0.105718
N	-1.995330	1.816563	0.358256
N	-3.331129	0.445952	-0.585896
N	2.743483	1.440989	1.541214
H	2.540122	0.424923	1.397239
C	2.580646	2.089451	0.212183
H	3.247826	2.958236	0.186813
C	2.950859	1.113141	-0.901513
H	2.605521	1.536403	-1.844798
H	4.036859	0.997501	-0.947817
C	1.137181	2.625849	0.115560
O	0.467718	2.623516	1.197689
O	0.761582	3.049479	-0.996029
H	2.027683	1.829463	2.169435
H	3.676254	1.550283	1.938241
H	-3.707061	-0.403886	-0.981712
Se	2.160177	-0.691588	-0.620267

Sec

Cys

Product:

24

-710.570963

Au	0.599916	-0.859021	-0.074465
Cl	0.355500	3.116046	-0.665533
C	2.461743	-0.119287	0.185415
C	4.141354	1.382391	0.315160
H	3.700882	-1.735771	0.642929
H	4.598577	2.358608	0.274046
H	5.676077	-0.152016	0.821174
C	4.670015	0.155778	0.582889
N	3.621573	-0.739003	0.495683
N	2.797757	1.182593	0.078264
N	-1.895978	1.374268	0.701269
H	-1.382104	0.560583	1.065730
C	-2.932489	0.899649	-0.248436
H	-3.264941	1.777815	-0.814255
C	-2.352440	-0.116785	-1.222878
H	-3.171490	-0.476717	-1.847124
H	-1.610759	0.358312	-1.867837
C	-4.150218	0.387115	0.561588
O	-4.165947	0.679859	1.788052
H	-2.361127	1.818804	1.498352
H	-1.199709	2.016765	0.261681
H	2.106327	1.909211	-0.152996
O	-5.027923	-0.229690	-0.089782
S	-1.604306	-1.587827	-0.390001

Protonated branch - one-step mechanism

Reactant:

25

-711.001708

Au	0.812677	-0.974500	-0.054545
Cl	-0.488070	-2.932438	-0.306909
C	1.852340	0.718815	0.074819
C	3.413692	2.280759	0.534002
H	0.595332	2.020556	-0.968518
H	4.331059	2.668683	0.948211
H	2.309854	3.897084	-0.524394
C	2.423507	2.878873	-0.186434
N	1.488012	1.902912	-0.453102
N	3.036723	0.960649	0.677591
N	-2.547343	-0.273193	-1.261055
H	-1.913925	-0.002555	-2.026227
C	-2.985048	0.983347	-0.592419
H	-3.838577	1.361246	-1.166067
C	-3.432531	0.733466	0.837267
H	-3.824930	1.662492	1.250124
H	-4.223949	-0.020041	0.864479
C	-1.846813	2.023035	-0.727644
O	-0.984309	1.773388	-1.623789
O	-1.890335	3.010546	0.031264
H	-3.326230	-0.822730	-1.627557
H	-2.003541	-0.877231	-0.625659
S	-2.103464	0.087179	1.920365
H	-1.320432	1.184005	1.866599
H	3.570998	0.256751	1.168279

Sec

Product:

24

-709.723625

Au	0.713324	-0.790751	-0.029427
Cl	0.683480	3.209007	-0.827296
C	2.604460	-0.098567	0.207485
C	4.337112	1.344994	0.289944
H	3.774562	-1.733053	0.770927
H	4.830794	2.300721	0.208098
H	5.805199	-0.216258	0.900905
C	4.815303	0.115389	0.629166
N	3.735468	-0.743442	0.569401
N	2.990881	1.182519	0.039630
N	-1.611097	1.652354	0.668907
H	-1.133443	0.810701	1.020628
C	-2.735866	1.244047	-0.209089
H	-3.024743	2.137756	-0.775797
C	-2.308451	0.166421	-1.191161
H	-3.184613	-0.130684	-1.767571
H	-1.546369	0.543720	-1.874658
C	-3.945437	0.860306	0.680755
O	-3.865469	1.185324	1.896649
H	-1.996768	2.140805	1.483021
H	-0.897278	2.236539	0.178450
H	2.332897	1.923773	-0.240561
O	-4.908286	0.306441	0.097295
Se	-1.622102	-1.484337	-0.319248

Protonated branch - one-step mechanism

Reactant:

25

-710.147150

Au	1.120156	-0.897645	-0.103796
Cl	0.121661	-3.008803	-0.463734
C	1.899936	0.921600	0.123984
C	3.148269	2.687286	0.767591
H	0.614189	2.042859	-1.082824
H	3.940379	3.198239	1.292082
H	1.965982	4.139666	-0.434281
C	2.182168	3.144704	-0.077632
N	1.439169	2.047100	-0.454576
N	2.950814	1.324905	0.870809
N	-2.173384	-0.586536	-1.626615
H	-1.489322	-0.284955	-2.334199
C	-2.834933	0.639693	-1.102408
H	-3.666456	0.860251	-1.781424
C	-3.391480	0.422542	0.292415
H	-3.907756	1.324395	0.616925
H	-4.093312	-0.415106	0.308013
C	-1.834201	1.815643	-1.207133
O	-0.819745	1.606679	-1.939767
O	-2.121424	2.856345	-0.585171
H	-2.832528	-1.252650	-2.031736
H	-1.639621	-1.071679	-0.889393
H	-1.304118	1.236426	1.512316
H	3.513481	0.699464	1.431019
Se	-2.019614	-0.041311	1.628475

Cys

TS:

25

-710.986972

Au	-0.221995	-0.765229	-0.188960
Cl	1.524676	-2.247381	1.159354
C	-2.088151	-0.052487	-0.022441
C	-4.319378	0.294693	-0.036623
H	-1.611571	1.846182	0.670587
H	-5.356854	0.042702	-0.190691
H	-4.145610	2.379778	0.719279
C	-3.724665	1.436584	0.407509
N	-2.366387	1.195698	0.404422
N	-3.294234	-0.597848	-0.290294
N	2.023606	0.857216	1.775862
H	1.171728	1.240069	2.214662
C	2.264643	1.676663	0.553549
H	2.943233	2.482023	0.855166
C	2.965770	0.889360	-0.543944
H	3.463693	1.582578	-1.221468
H	3.725377	0.232596	-0.113755
C	0.935446	2.365297	0.150041
O	0.886013	2.855226	-0.995649
O	0.047924	2.400700	1.053818
H	2.799618	0.907994	2.436953
H	1.854678	-0.150599	1.569571
S	1.916073	-0.192527	-1.598175
H	1.322353	0.821988	-2.260970
H	-3.420119	-1.539862	-0.633530

Product:

25

-711.013545

Au	0.593620	-0.825648	-0.123751
Cl	0.414103	3.035495	-0.697971
C	2.469276	-0.159254	0.215189
C	4.194269	1.281159	0.419140
H	3.634275	-1.822991	0.697294
H	4.686386	2.241029	0.404658
H	5.655835	-0.311475	0.960334
C	4.669987	0.033995	0.691225
N	3.594852	-0.822623	0.558397
N	2.853686	1.130695	0.134092
N	-1.811067	1.446332	0.773920
H	-1.333457	0.633400	1.183302
C	-2.885702	0.994480	-0.137072
H	-3.308846	1.888707	-0.608695
C	-2.339470	0.066014	-1.220593
H	-3.169957	-0.208612	-1.872919
H	-1.604137	0.609516	-1.816170
C	-3.973077	0.347241	0.703025
O	-3.950833	0.299446	1.917448
H	-2.176538	2.013300	1.542037
H	-1.084272	2.011589	0.260028
S	-1.614107	-1.486689	-0.543873
H	2.194026	1.878448	-0.116443
O	-4.954318	-0.131500	-0.054376
H	-5.636103	-0.529348	0.515479

Sec

TS:

25

-710.132447

Au	-0.382087	-0.776856	-0.035117
Cl	1.268041	-2.153991	1.516861
C	-2.262381	-0.072853	-0.091419
C	-4.476340	0.264006	-0.383866
H	-1.870192	1.850413	0.585972
H	-5.488155	0.002360	-0.651166
H	-4.393608	2.375957	0.309590
C	-3.938557	1.423658	0.086015
N	-2.589576	1.188658	0.253646
N	-3.428227	-0.632732	-0.481451
N	1.722504	0.989236	2.029899
H	0.838289	1.349686	2.419942
C	2.011798	1.817298	0.824715
H	2.613825	2.662752	1.177961
C	2.849324	1.076934	-0.201866
H	3.304637	1.792269	-0.885268
H	3.645423	0.511354	0.287321
C	0.683560	2.431346	0.314431
O	0.698402	2.929557	-0.827635
O	-0.274754	2.409922	1.144666
H	2.460838	1.054371	2.731880
H	1.582050	-0.020920	1.818235
Se	1.929406	-0.234517	-1.359827
H	1.321626	0.797761	-2.209800
H	-3.512894	-1.587247	-0.801954

Product:

25

-710.166563

Au	0.710676	-0.770809	-0.048326
Cl	0.724112	3.131098	-0.883674
C	2.611350	-0.131478	0.243037
C	4.382664	1.262385	0.346427
H	3.718121	-1.790644	0.858888
H	4.906300	2.201817	0.262126
H	5.788914	-0.331558	1.015730
C	4.815982	0.024637	0.715250
N	3.713223	-0.803440	0.642081
N	3.038644	1.135007	0.065975
N	-1.524358	1.711316	0.714802
H	-1.067746	0.874503	1.103408
C	-2.684630	1.312853	-0.111815
H	-3.060901	2.221690	-0.597085
C	-2.281844	0.303565	-1.180460
H	-3.158374	0.072786	-1.786239
H	-1.517518	0.740042	-1.824248
C	-3.772513	0.803718	0.819089
O	-3.697840	0.848192	2.031579
H	-1.802798	2.306085	1.497771
H	-0.800008	2.223412	0.144819
H	2.406824	1.886745	-0.240645
O	-4.817597	0.341039	0.142015
H	-5.499151	0.040072	0.768678
Se	-1.625356	-1.413171	-0.432379

Cys

Protonated branch - two-step mechanism

TS1:

25

-710.977075

Au	1.213612	-0.861005	0.021440
Cl	-0.077783	-2.834459	0.101314
C	2.192136	0.867102	-0.087966
C	3.774536	2.463406	-0.271928
H	0.611309	2.214230	0.016983
H	4.774747	2.855139	-0.369426
H	2.303413	4.132995	-0.194172
C	2.566301	3.086893	-0.186616
N	1.623232	2.087769	-0.076889
N	3.513783	1.109436	-0.209259
N	-2.247680	-0.629949	-0.958567
H	-1.731653	0.196132	-1.286298
C	-3.101609	-0.277193	0.219403
H	-3.444742	-1.221209	0.644915
C	-2.258446	0.477943	1.246065
H	-2.876517	0.651579	2.130093
H	-1.403661	-0.135914	1.542740
C	-4.340870	0.509027	-0.271660
O	-5.445199	-0.045220	-0.235985
O	-4.121711	1.704345	-0.701227
H	-2.792917	-0.998471	-1.741005
H	-1.557006	-1.357220	-0.693494
S	-1.649812	2.085547	0.584286
H	-2.937755	2.109316	-0.240913
H	4.216434	0.383031	-0.247160

Intermediate:

25

-710.986702

Au	1.201958	-0.867008	-0.014170
Cl	-0.095549	-2.838851	-0.084785
C	2.207098	0.849334	0.057053
C	2.630003	3.060387	0.052243
H	4.203342	0.331841	0.385709
H	2.394628	4.110735	-0.019043
H	4.815100	2.794001	0.403073
C	3.814151	2.418733	0.259048
N	3.523985	1.069403	0.256745
N	1.670874	2.078278	-0.067832
N	-2.559011	-0.833420	-0.730323
H	-2.184358	-0.129355	-1.394310
C	-2.984489	-0.106632	0.503048
H	-3.086582	-0.848573	1.296427
C	-1.909667	0.927092	0.853197
H	-2.263694	1.510826	1.707120
H	-1.006227	0.393551	1.166357
C	-4.376713	0.507677	0.286830
O	-5.374065	-0.007965	0.761440
O	-4.443009	1.614285	-0.433575
H	-3.310313	-1.366060	-1.173477
H	-1.791710	-1.499412	-0.514211
S	-1.528550	2.018987	-0.580708
H	-3.501964	1.939702	-0.669635
H	0.661608	2.223156	-0.237487

Sec

Protonated branch - two-step mechanism

TS1:

25

-710.126618

Au	0.939278	0.970332	-0.025902
Cl	-0.533369	2.816932	0.088013
C	2.184394	-0.583880	-0.078539
C	4.024560	-1.875180	-0.281797
H	0.921731	-2.172027	0.391992
H	5.065360	-2.088211	-0.468281
H	2.933368	-3.753793	0.202360
C	2.981389	-2.687582	0.045690
N	1.875738	-1.872817	0.162804
N	3.507340	-0.597493	-0.349891
N	-2.533801	0.698038	1.570232
H	-1.969113	1.185337	0.850679
C	-2.737533	-0.749884	1.268392
H	-3.400492	-1.121523	2.057634
C	-3.414268	-0.947837	-0.076963
H	-3.817979	-1.961465	-0.104910
H	-4.247770	-0.249136	-0.177723
C	-1.380371	-1.451706	1.515510
O	-0.838841	-1.275473	2.606513
O	-0.902771	-2.196615	0.566879
H	-2.043824	0.804620	2.463469
H	-3.428169	1.187970	1.644378
H	-1.277498	-1.720992	-0.536065
H	4.041434	0.230748	-0.574992
Se	-2.172758	-0.733134	-1.606513

Intermediate:

25

-710.137969

Au	1.387648	-0.929947	-0.028563
Cl	0.186095	-2.952756	-0.241404
C	2.347174	0.803660	0.165008
C	2.727127	3.021235	0.277998
H	4.341236	0.308330	0.536448
H	2.473322	4.069220	0.246774
H	4.903952	2.777477	0.688886
C	3.915691	2.391427	0.494524
N	3.651898	1.038669	0.419714
N	1.792572	2.027841	0.080800
N	-2.502097	-1.204149	-0.594565
H	-2.230979	-0.499415	-1.306699
C	-2.874696	-0.478974	0.656007
H	-2.893208	-1.220104	1.457372
C	-1.825575	0.594378	0.942572
H	-2.157914	1.189855	1.795302
H	-0.886622	0.103635	1.214158
C	-4.309466	0.058517	0.535265
O	-5.239082	-0.510906	1.079083
O	-4.499681	1.158199	-0.176352
H	-3.247494	-1.800893	-0.959238
H	-1.670038	-1.806063	-0.433709
H	-3.617877	1.538305	-0.502493
H	0.790607	2.160106	-0.117905
Se	-1.504731	1.773114	-0.625008

TS2:

25

-710.981101

Au	0.904237	0.527026	-0.016654
Cl	-0.506588	2.561495	0.275991
C	2.618630	-0.516716	0.090386
C	4.670241	-1.363489	-0.376547
H	2.303499	-1.842847	1.669470
H	5.605728	-1.444473	-0.907322
H	4.584548	-2.873747	1.255390
C	4.171977	-2.060990	0.678698
N	2.924412	-1.525205	0.938313
N	3.704626	-0.432654	-0.711736
N	-2.619612	0.440039	1.217725
H	-1.891165	-0.294364	1.227433
C	-3.487483	0.174506	0.049356
H	-4.225609	0.981861	-0.016883
C	-2.610415	0.145133	-1.210138
H	-3.226480	-0.137847	-2.067828
H	-2.254674	1.164184	-1.385401
C	-4.215542	-1.136750	0.306621
O	-4.064004	-1.792117	1.317670
O	-5.064644	-1.543413	-0.636418
H	-3.123620	0.447432	2.105814
H	-2.108833	1.335478	1.086359
S	-1.192891	-0.997815	-1.017724
H	-5.110246	-0.931898	-1.388764
H	3.789166	0.239572	-1.461264

Sec

TS2:

25

-710.127636

Au	-0.687586	-0.956208	0.094549
Cl	0.224156	-3.176774	0.649631
C	-2.092581	0.459942	-0.087734
C	-3.920526	1.615280	-0.768194
H	-1.574875	1.875815	1.349378
H	-4.796591	1.811406	-1.366081
H	-3.628452	3.245157	0.718930
C	-3.351781	2.313765	0.250465
N	-2.244507	1.585882	0.644537
N	-3.133787	0.493903	-0.950648
N	3.026564	1.472113	1.365335
H	2.801539	0.455462	1.231287
C	2.519049	2.158055	0.152985
H	3.051497	3.110857	0.053198
C	2.757267	1.276140	-1.075133
H	2.241902	1.720678	-1.926385
H	3.828341	1.258048	-1.291102
C	1.057530	2.483754	0.392860
O	0.498597	2.327007	1.465093
H	2.568787	1.807349	2.217114
H	4.038028	1.575442	1.463038
H	-3.312372	-0.227479	-1.634983
O	0.492992	3.005642	-0.686604
H	-0.427457	3.254715	-0.494389
Se	2.130411	-0.579646	-0.754913

S. 5 Used basis sets of pseudoorbitals and standard SDD pseudopotentials

Consistent basis set (pseudoorbitals) for standard SDD pseudopotentials to triple-zeta AO basis set of first and second row atoms [6-311++G(2df,2pd)]

(in Gaussian 09 format)

S:

```
S   3  1.00
      6.83351800          -0.438750000E-01
      2.07773800           0.319894000
      0.419121000         -0.661233000
S   1  1.00
     0.153237000          1.00000000
S   1  1.00
     0.070
1.00000000
P   3  1.00
      1.81713900          -0.792270000E-01
     0.855070000          0.263671000
     0.312053000          0.580682000
P   1  1.00
     0.101687000          1.00000000
P   1  1.00
     0.0298100
1.00000000
P   1  1.00
     0.0100000                   1.00000000
D   1  1.00
    2.7009               1.00000000
D   1  1.00
    0.2433               1.00000000
F   1  1.00
    0.6961               1.00000000
****
```

Cl:

```
S 3 1.0
   14.073076000          0.020345000
    2.331565000          -
0.289223000
    0.507100000          0.630367000
S 1 1.0
    0.3648000
          1.0000000000
S 1 1.0
    0.0912000
          1.0000000000
S 1 1.0
    0.0483000
          1.0000000000
P 3 1.0
    3.353129000          -
0.041552000
    0.785686000          0.399748000
    0.267454000          0.591829000
P 1 1.0
    0.078275000          1.000000000
P 1 1.0
    0.015477000          1.000000000
P 1 1.0
    0.0070000            1.000000000
D    1 1.00
    1.50000          1.000000000
D    1 1.00
    0.3750000        1.000000000
F    1 1.00
    0.7000000        1.000000000
****
```

Se :

```
S   3   1.00
      3.5881800          0.2496300
      2.2397110         -0.5814600
      0.3437730          0.7289380
S   1   1.00
      0.1313990          1.0000000
S   1   1.00
      0.0656995          1.0000000
P   3   1.00
      1.5094270          0.1952710
      0.8751060         -0.2539150
      0.2908260         -0.5904870
P   1   1.00
      0.1002210          1.0000000
P   1   1.00
      0.0325160          1.0000000
P   1   1.00
      0.0162580          1.0000000
D   1
      0.6383506          1.0000000
D   1
      0.2312957          1.0000000
F   1
      0.6630066          1.0000000
****
```

Au:

```
S   2   1.00
     30.1965370          0.0047330
      9.7259730         -0.3543820
S   1   1.00
      5.0804060          1.0000000
S   1   1.00
      1.7226570          1.0000000
S   1   1.00
      0.7264590          1.0000000
S   1   1.00
      0.0903540          1.0000000
S   1   1.00
      0.0221060          1.0000000
S   1   1.00
      0.0064150          1.0000000
S   1   1.00
      0.0032075          1.0000000
P   4   1.00
     13.8382190          0.0361790
      5.1957870         -0.3283030
      1.7980450          0.6653880
      0.6661050          0.5526660
P   1   1.00
      0.1543360          1.0000000
P   1   1.00
      0.0340000          1.0000000
P   1   1.00
      0.0170000          1.0000000
D   2   1.00
      6.3370010         -0.0441030
      1.4806970          0.4621150
D   1   1.00
      0.5283820          1.0000000
D   1   1.00
      0.1711170          1.0000000
D   1   1.00
      0.0455120          1.0000000
D   1   1.00
      0.0227560          1.0000000
F   1   1.00
      1.5343593          1.0000000
F   1   1.00
      0.6118593          1.0000000
G   1   1.00
      1.5117593          1.0000000
****
```

Standard SDD pseudopotentials:
(used in combination with above written atomic pseudoorbitals)

```
S     0
S-ECP     3     10
f potential
  1
2      1.000000000          0.000000000
s-f potential
  1
2      3.743891640          37.974819000
p-f potential
  1
2      3.086087440          18.790529310
d-f potential
  1
2      4.862414000          -7.837964000
```

```
SE     0
SE-ECP     4     28
g potential
  1
2      1.000000000          0.000000000
s-g potential
  1
2      4.237057000          79.663345000
p-g potential
  1
2      2.910334000          31.560993000
d-g potential
  1
2      2.335701000          30.804610000
f-g potential
  1
2      2.254639000          -6.546875000
```

```
CL     0
CL-ECP     3     10
f potential
  1
2      1.000000000          0.000000000
s-f potential
  2
2      6.394300000          33.136632000
2      3.197100000          16.270728000
p-f potential
  2
2      5.620700000          24.416993000
2      2.810300000           7.683050000
d-f potential
  1
2      5.338100000          -8.587649000
```

```
AU     0
AU-ECP     4     60
g-ul potential
  1
2      1.000000000          0.000000000
s-ul potential
  2
2     13.205100000          426.709840000
2      6.602550000          35.938824000
p-ul potential
  2
2     10.452020000          261.161023000
2      5.226010000          26.626284000
d-ul potential
  2
2      7.851100000          124.756831000
2      3.925550000          15.772260000
f-ul potential
  2
2      4.789800000          30.568475000
2      2.394910000           5.183774000
```