A Computational Investigation of the Binding of the Selenium Analogues of Ergothioneine and Ovothiol to Cu(I) and Cu(II) and the Effect of Binding on the Redox Potential of the Cu(II)/Cu(I) Redox Couple.

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Supporting Information 12 pages in Total

Table S1. The Boltzmann equation used for the calculation of the relative populations of the Cu-OSeH and Cu-ESeH complexes. N_i/N is the relative population of species *i*, μ_i is the relative chemical potential in solution for species $_i$, g_i is the degeneracy, and $\sum g_i e^{\mu_i/RT}$ is the partition function.

$$\frac{N_i}{N} = \frac{g_i e^{\mu_i/RT}}{\sum g_i e^{\mu_i/RT}}$$

Table S2. All xyz-coordinates of the selenium containing compounds optimized at the BP86/6-311+G(2df,p) level of theory.

cis-Cu(II)$(OSe)_2$

C	0	-0.00702	-0.45636	0.13559
N	0	1.33486	-0.17131	-0.15877
C	0	-0.62851	0.77689	0.2006
C	0	1.46922	1.17963	-0.26276
N	0	0.30313	1.77775	-0.04527
H	0	2.41389	1.66537	-0.49199
C	0	-0.39768	7.3503	-0.17373
N	0	0.94938	7.20256	0.18984
C	0	-0.88627	6.06036	-0.26718
C	0	1.21502	5.87205	0.30425
N	0	0.12855	5.1589	0.02886
H	0	2.1912	5.4844	0.58294
Se	0	-2.3743	1.46945	0.47786
Se	0	-2.53596	5.19442	-0.63179
C	0	2.40096	-1.14841	-0.31111
H	0	3.33459	-0.62286	-0.54844
H	0	2.54309	-1.72075	0.61816
H	0	2.17292	-1.84962	-1.12791
C	0	1.90126	8.28271	0.39404
H	0	2.87013	7.85431	0.68034
H	0	2.03188	8.86892	-0.52824
H	0	1.56145	8.95497	1.19619
C	0	-0.53918	-1.83605	0.30392
H	0	-0.38186	-2.46249	-0.59103
H	0	-0.09113	-2.36407	1.1636
H	0	-1.62183	-1.77487	0.48047
C	0	-1.05814	8.66908	-0.37289
H	0	-1.0115	9.30603	0.52724

H	0	-0.62265	9.24211	-1.20989
H	0	-2.11845	8.49848	-0.60457
Cu	0	-0.94082	3.40927	-0.03797

trans-Cu(II)$(OSe)_2$

C	0	-0.09587	-0.49092	-0.01138
N	0	1.28571	-0.23535	-0.00311
C	0	-0.69194	0.75619	-0.02433
C	0	1.47575	1.10989	-0.01062
N	0	0.29857	1.72636	-0.02361
H	0	2.45292	1.58395	-0.00659
C	0	-1.20039	7.32199	-0.07121
N	0	-2.58199	7.06649	-0.07953
C	0	-0.60437	6.07486	-0.0588
C	0	-2.77208	5.72126	-0.07222
N	0	-1.59492	5.10473	-0.05969
H	0	-3.74927	5.24724	-0.07624
Se	0	-2.43265	1.51068	-0.04217
Se	0	1.13632	5.32033	-0.04123
C	0	2.33702	-1.24078	0.0111
H	0	3.31149	-0.73676	0.0153
H	0	2.25931	-1.87117	0.9095
H	0	2.27283	-1.88244	-0.88037
C	0	-3.63325	8.07196	-0.09362
H	0	-4.60775	7.56799	-0.09754
H	0	-3.56883	8.7137	0.79778
H	0	-3.55572	8.70228	-0.99209
C	0	-0.68005	-1.85951	-0.00629
H	0	-0.38544	-2.45022	-0.89084
H	0	-0.39856	-2.43801	0.89053
H	0	-1.77514	-1.77138	-0.01496
C	0	-0.61616	8.69056	-0.07586
H	0	-0.89763	9.26936	-0.97249
H	0	-0.91074	9.28101	0.80889
H	0	0.47893	8.60239	-0.06722
Cu	0	-0.6482	3.41553	-0.04169

Cis-δ-Cu(II)$(ESe)_2$

C	0	-2.48612	1.56109	0.37509
N	0	-1.73277	0.43806	0.04735

C	0	-3.81652	1.22905	0.2697
C	0	-2.58479	-0.56061	-0.23107
N	0	-3.86292	-0.11152	-0.11422
H	0	-4.71637	1.81799	0.41339
C	0	2.48601	1.56145	-0.37537
N	0	1.73267	0.43813	-0.0486
C	0	3.81641	1.22934	-0.27023
C	0	2.5847	-0.56079	0.2289
N	0	3.86282	-0.1116	0.1124
H	0	4.71625	1.81842	-0.41336
Se	0	-1.82355	-2.2398	-0.60668
Se	0	1.82348	-2.24033	0.603
C	0	1.8713	2.86604	-0.75655
H	0	1.21923	2.75543	-1.63754
H	0	1.25543	3.27167	0.06148
H	0	2.64828	3.60479	-0.99765
C	0	-1.87143	2.86536	0.75742
H	0	-1.21935	2.75397	1.63831
H	0	-1.25556	3.27172	-0.06026
H	0	-2.64841	3.60388	0.99918
H	0	4.69656	-0.67338	0.24929
H	0	-4.69665	-0.67318	-0.25165
Cu	0	-0.00004	-0.64665	-0.00111

Cis-*ε*-Cu(II)$(ESe)_2$

C	0	3.6884	1.44882	0.08099
N	0	3.83208	0.0554	0.07928
C	0	2.33169	1.66768	0.05551
H	0	4.70819	-0.45758	0.09453
C	0	2.5926	-0.51237	0.05364
N	0	1.66536	0.45198	0.03887
H	0	1.80445	2.617	0.04851
C	0	-3.68878	1.44811	-0.08047
N	0	-3.83218	0.05466	-0.07935
C	0	-2.33221	1.66724	-0.0499
H	0	-4.7081	-0.4585	-0.09871
C	0	-2.5927	-0.51286	-0.04882
N	0	-1.66572	0.45168	-0.03009
H	0	-1.80521	2.61667	-0.0406
Se	0	1.95271	-2.28191	0.03578

Se	0	-1.95246	-2.28228	-0.03132
C	0	-4.8534	2.37868	-0.1097
H	0	-5.47117	2.24169	-1.01343
H	0	-5.5108	2.24817	0.76663
H	0	-4.49708	3.41768	-0.10554
C	0	4.85293	2.37962	0.10654
H	0	5.4731	2.24339	1.00875
H	0	5.50804	2.2486	-0.77142
H	0	4.4964	3.41855	0.10258
Cu	0	-0.00006	-0.70237	0.00379

Trans-δ-Cu(II)$(ESe)_2$

C	0	3.07189	0.8703	0.06008
N	0	1.92847	0.0772	0.06055
C	0	4.15753	0.02783	0.06048
C	0	2.29995	-1.21297	0.06042
N	0	3.65689	-1.27694	0.05991
H	0	5.22227	0.23496	0.0606
C	0	-3.07185	-0.87032	0.06005
N	0	-1.92842	-0.07722	0.06052
C	0	-4.15749	-0.02785	0.06042
C	0	-2.29991	1.21294	0.06039
N	0	-3.65684	1.27692	0.05986
H	0	-5.22223	-0.23498	0.06054
Se	0	0.92525	-2.49206	0.0606
Se	0	-0.9252	2.49204	0.06057
C	0	-3.02353	-2.36071	0.05978
H	0	-2.49292	-2.74178	-0.82705
H	0	-2.49312	-2.74205	0.9466
H	0	-4.03959	-2.77901	0.05961
C	0	3.02357	2.36068	0.0598
H	0	2.49298	2.74175	-0.82704
H	0	2.49315	2.74203	0.94661
H	0	4.03964	2.77899	0.05964
H	0	-4.19963	2.13407	0.05953
H	0	4.19968	-2.13409	0.05959
Cu	0	0.00002	-0.00001	0.06067

Trans-ε-Cu(II)$(ESe)_2$

C	0	-4.15161	-0.36975	0.0174

N	0	-3.74771	0.97262	0.01758
C	0	-2.9864	-1.09682	0.01706
H	0	-4.35871	1.78361	0.01829
C	0	-2.38583	1.02617	0.01627
N	0	-1.90881	-0.22597	0.01582
H	0	-2.85488	-2.17437	0.01706
C	0	4.15399	0.3687	0.01728
N	0	3.75009	-0.97368	0.01759
C	0	2.98878	1.09576	0.01696
H	0	4.36109	-1.78466	0.01837
C	0	2.38821	-1.02723	0.01624
N	0	1.91119	0.22492	0.01572
H	0	2.85726	2.17332	0.01691
Se	0	-1.12816	2.42062	0.01577
Se	0	1.13054	-2.42168	0.01582
C	0	5.58692	0.7793	0.0177
H	0	6.12339	0.41011	0.90818
H	0	6.12398	0.4102	-0.87246
H	0	5.65737	1.87529	0.01779
C	0	-5.58454	-0.78036	0.0179
H	0	-6.12098	-0.41111	0.90838
H	0	-6.12163	-0.41131	-0.87226
H	0	-5.65499	-1.87635	0.01805
Cu	0	0.00119	-0.00053	0.01564

$Cu(I)(ESeH)_3$

C	0	4.10529	-1.86633	0.95101
N	0	2.96856	-1.41599	0.27801
C	0	4.03847	-3.23138	0.91866
H	0	2.71368	-0.43162	0.08776
C	0	2.21569	-2.45042	-0.16967
N	0	2.87595	-3.56693	0.232
H	0	4.71085	-3.98094	1.32044
H	0	-4.96635	-0.02551	-0.25016
N	0	-4.31136	-0.75459	0.02208
C	0	-4.63341	-1.92426	0.71528
C	0	-2.98721	-0.71071	-0.29326
C	0	-3.45658	-2.61087	0.82752
N	0	-2.4687	-1.85244	0.21131
H	0	-3.24474	-3.56819	1.29016

C	0	1.14501	2.95084	-0.32282
N	0	-0.12269	3.09576	0.13442
N	0	1.77204	4.1108	0.00209
C	0	-0.3085	4.34105	0.73657
H	0	-0.83999	2.36368	-0.00586
C	0	0.89805	4.97799	0.65015
H	0	1.20292	5.96159	0.98915
C	0	-6.01365	-2.23833	1.17745
H	0	-6.38912	-1.47854	1.88133
H	0	-6.71929	-2.29495	0.33335
H	0	-6.02538	-3.20821	1.69076
C	0	5.1157	-0.94478	1.54072
H	0	5.56325	-0.29554	0.77199
H	0	4.66927	-0.29637	2.31104
H	0	5.9227	-1.52234	2.00928
C	0	-1.60999	4.77401	1.31672
H	0	-2.40432	4.78625	0.55407
H	0	-1.93294	4.10325	2.12845
H	0	-1.51927	5.78695	1.72914
Se	0	0.62878	-2.41307	-1.16922
Se	0	1.90877	1.50897	-1.24831
Se	0	-2.13205	0.64892	-1.26301
H	0	2.55109	-4.50709	0.02277
H	0	2.74252	4.29995	-0.2336
H	0	-1.47455	-2.1092	0.08274
Cu	0	0.13657	-0.08259	-1.26226

$Cu(I)(OSeH)_3$

C	5.74748	-2.19247	-0.49407
H	6.2806	-2.74757	0.29535
H	6.49275	-1.85986	-1.23565
C	4.94762	-1.06372	0.04995
N	5.50429	-0.00412	0.77152
C	3.57826	-0.82476	-0.02793
C	4.53378	0.85471	1.12708
N	3.3741	0.37264	0.64934
H	4.67096	1.76436	1.70032
C	-2.9945	-1.35364	0.10137
C	-4.19493	-2.0344	0.26286
N	-2.75315	-0.72326	1.31742

C	-4.93942	-2.89515	-0.69362
N	-4.6256	-1.78661	1.5701
C	-3.7363	-0.9909	2.18925
H	-5.94034	-2.49602	-0.92666
H	-5.06523	-3.92333	-0.31674
H	-3.80465	-0.64042	3.21316
H	-0.92617	5.43951	1.42784
C	-0.18023	4.78477	0.94838
H	0.55931	5.42987	0.44593
C	-0.80219	3.80758	0.01612
N	-1.55981	4.18349	-1.09825
C	-0.77836	2.42007	0.02844
C	-1.9829	3.07783	-1.73787
N	-1.52177	2.01334	-1.07232
H	-2.58538	3.06037	-2.63979
H	5.06432	-2.89158	-0.99508
H	-4.36911	-2.94807	-1.63084
H	0.33775	4.22824	1.74113
C	6.92064	0.14768	1.09678
H	7.25987	-0.70044	1.70698
H	7.51584	0.18959	0.17456
H	7.06187	1.07732	1.66036
C	-5.8433	-2.32019	2.17808
H	-6.72467	-1.97917	1.61833
H	-5.81504	-3.41822	2.1744
H	-5.91224	-1.96479	3.21278
C	-1.84394	5.55636	-1.51338
H	-2.39446	6.08411	-0.7229
H	-0.90641	6.08971	-1.72086
H	-2.45375	5.53471	-2.42406
Se	0.05386	1.20993	1.23761
Se	-1.82457	-1.29036	-1.39006
Se	2.21769	-1.83365	-0.86128
Cu	0.25643	-0.70324	-0.30612
H	-1.67345	0.99439	-1.32223
H	2.43664	0.7983	0.76482
H	-1.90553	-0.13945	1.49291

ESe^-

C	0	-1.33424	0.34264	-1.687

N	0	-1.22439	-0.53608	-0.61595
C	0	-0.02408	0.5672	-2.05782
H	0	-1.96959	-0.94464	-0.05994
C	0	0.11761	-0.81122	-0.37537
N	0	0.86433	-0.13277	-1.26265
H	0	0.32449	1.20793	-2.86996
Se	0	0.62171	-1.97816	1.02109
C	0	-2.63494	0.84905	-2.21425
H	0	-3.29533	0.03881	-2.58004
H	0	-3.21326	1.41659	-1.45934
H	0	-2.45038	1.52751	-3.06186

ESeH

C	0	-1.3215	0.35009	-1.69488
N	0	-1.22439	-0.53366	-0.61785
C	0	-0.03747	0.59643	-2.0852
H	0	-1.99499	-0.92486	-0.08446
C	0	0.08043	-0.85114	-0.31803
N	0	0.79721	-0.13592	-1.24435
H	0	0.34248	1.22525	-2.88259
Se	0	0.70538	-1.95771	0.99605
C	0	-2.62299	0.8504	-2.21884
H	0	-3.26403	0.0256	-2.57152
H	0	-3.18559	1.40482	-1.44959
H	0	-2.45208	1.52904	-3.06506
H	0	1.81096	-0.17213	-1.27004

ESeSeE

C	0	4.78199	-1.3467	-1.11102
N	0	3.43181	-1.6006	-0.98814
C	0	5.40541	-2.47332	-0.59277
H	0	2.63472	-0.96278	-1.18787
C	0	3.30554	-2.82636	-0.38123
N	0	4.48334	-3.38237	-0.12584
H	0	6.47428	-2.66621	-0.52508
C	0	-1.30344	0.34735	-1.68374
N	0	-1.27829	-0.4907	-0.58264
C	0	0.02821	0.50807	-2.01865
H	0	-2.08329	-0.86033	-0.08357
C	0	0.03074	-0.78889	-0.28981

N	0	0.84464	-0.18681	-1.15108
H	0	0.43804	1.09265	-2.83899
Se	0	1.62568	-3.65755	-0.06664
Se	0	0.53572	-1.91676	1.1664
C	0	-2.55993	0.89303	-2.2736
H	0	-3.24218	0.09303	-2.60558
H	0	-3.11044	1.52693	-1.5587
H	0	-2.31979	1.51025	-3.14969
C	0	5.32887	-0.08236	-1.68497
H	0	4.9979	0.07467	-2.72509
H	0	5.01949	0.80154	-1.10284
H	0	6.42697	-0.11784	-1.68389

OSe^-

C	0	-1.02073	1.77877	-0.48221
N	0	-1.54959	0.49054	-0.35167
C	0	-0.21577	1.98868	0.64311
C	0	-1.05156	-0.01532	0.82409
N	0	-0.25791	0.83977	1.44436
H	0	-1.31358	-1.01845	1.1649
Se	0	0.77777	3.55849	1.043
C	0	-2.43655	-0.18057	-1.27186
H	0	-2.67264	-1.17984	-0.87542
H	0	-3.38245	0.37472	-1.40199
H	0	-1.97419	-0.3014	-2.26786
C	0	-1.31415	2.67775	-1.62991
H	0	-0.9864	2.26863	-2.60649
H	0	-2.38772	2.93662	-1.7252
H	0	-0.75328	3.60886	-1.44324

OSeH

C	0	-0.94948	1.74493	-0.47148
N	0	-1.51521	0.48296	-0.34573
C	0	-0.10423	1.85862	0.62459
C	0	-0.99574	-0.07897	0.79627
N	0	-0.13647	0.71981	1.40056
H	0	-1.28451	-1.07495	1.12758
Se	0	1.05237	3.33977	0.99565
C	0	-2.47525	-0.12991	-1.25036
H	0	-2.71958	-1.13288	-0.87748

H	0	-3.40197	0.4615	-1.30157
H	0	-2.05671	-0.22302	-2.26386
C	0	-1.27856	2.68127	-1.58217
H	0	-0.95472	2.29964	-2.56566
H	0	-2.36096	2.88544	-1.64658
H	0	-0.76351	3.63541	-1.40501
H	0	0.29897	3.81404	2.18549

$OSeH_t$

C	0	-1.0203	1.77829	-0.47932
N	0	-1.53574	0.49181	-0.32938
C	0	-0.2046	2.04575	0.63147
C	0	-1.08434	-0.05352	0.81387
N	0	-0.28752	0.86747	1.39595
H	0	-1.32402	-1.04374	1.18212
Se	0	0.7969	3.51968	1.12207
C	0	-2.43214	-0.17362	-1.26689
H	0	-2.67121	-1.17511	-0.88864
H	0	-3.36128	0.40318	-1.37537
H	0	-1.95056	-0.26413	-2.25059
C	0	-1.32011	2.66109	-1.63535
H	0	-0.98681	2.23524	-2.59755
H	0	-2.39381	2.90083	-1.72438
H	0	-0.77323	3.60145	-1.47092
H	0	0.21029	0.76389	2.27726

OSeSeO

C	0	0.22713	0.75098	0.00362
N	0	-0.86384	-0.09857	-0.05971
C	0	-0.221	1.84734	0.73549
C	0	-1.89022	0.5099	0.63028
N	0	-1.53885	1.68149	1.11873
H	0	-2.86566	0.03765	0.7347
C	0	-1.24115	6.69338	-0.04673
N	0	-2.55772	6.94461	-0.39238
C	0	-0.88715	5.57365	-0.79463
C	0	-2.92128	5.99074	-1.31852
N	0	-1.9422	5.1498	-1.58097
H	0	-3.91731	5.97306	-1.75784
Se	0	0.78659	3.39261	1.20779

Se	0	0.80437	4.69916	-0.80844
C	0	-0.9233	-1.38496	-0.73594
H	0	-1.92923	-1.80452	-0.60645
H	0	-0.72455	-1.27173	-1.81232
H	0	-0.19096	-2.08807	-0.31088
C	0	-3.40423	8.00583	0.13001
H	0	-4.39385	7.92949	-0.33852
H	0	-3.52226	7.91259	1.22009
H	0	-2.98159	8.99598	-0.09877
C	0	1.53807	0.45105	-0.63347
H	0	1.93733	-0.5294	-0.32332
H	0	1.47584	0.45304	-1.73531
H	0	2.26035	1.22458	-0.33914
C	0	-0.48322	7.50743	0.94185
H	0	-0.50055	8.58282	0.69664
H	0	-0.87743	7.39193	1.96615
H	0	0.56326	7.1735	0.94794