Electronic Supplementary Information for

Theoretical Study of the Coordination Behavior of Formate and Formamidoximate with Dioxovanadium (V) Cation: Implications for Selectivity towards Uranyl

Nada Mehio¹, J. Casey Johnson,² Sheng Dai¹,², Vyacheslav S. Bryantsev²*

¹Department of Chemistry, University of Tennessee, Knoxville TN 37996 US
²Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge TN 37831 US

Email: bryantsevv@ornl.gov
Phone: (865) 576-4272
Fax: (865) 576 7956

Electronic supplementary information (ESI) available: Figure S1 showing structures of VO₂(HCOO)(H₂O)₃ complexes and relative energies in the gas phase and in aqueous solution, Table S1 listing relative electronic energies of VO₂(HCOO)(H₂O)₃ complexes at several levels of theory, and Cartesian coordinates of metal-ligand complexes accompanied with electronic energies of all species obtained with the B3LYP/aug-cc-pVDZ method and the MP2/aug-cc-pVDZ method, when available.
Figure S1. Structures of VO$_2$(HCOO)(H$_2$O)$_3$ complexes and relative energies in the gas phase and in aqueous solution (in parentheses) in units of kcal/mol.

Table S1. Relative gas phase electronic energies of five- and six-coordinate VO$_2$(HCOO)(H$_2$O)$_3$ in kcal/mol.$^a$ All energies are given relative to complex S1 in Figure S1.

<table>
<thead>
<tr>
<th>Theory</th>
<th>S2 (c.n. = 5)</th>
<th>S3 (c.n. = 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP2</td>
<td>-0.73</td>
<td>-1.53</td>
</tr>
<tr>
<td>MP2/aug-qz//MP2</td>
<td>-0.32</td>
<td>-1.46</td>
</tr>
<tr>
<td>CCSD(T)/MP2</td>
<td>-2.38</td>
<td>4.53</td>
</tr>
<tr>
<td>CCSD(T) + δMP2</td>
<td>-1.97</td>
<td>4.60</td>
</tr>
<tr>
<td>B3LYP</td>
<td>-1.74</td>
<td>7.49</td>
</tr>
<tr>
<td>CCSD(T)//B3LYP</td>
<td>-2.52</td>
<td>2.75</td>
</tr>
<tr>
<td>M06</td>
<td></td>
<td>3.53</td>
</tr>
<tr>
<td>M06-L</td>
<td></td>
<td>2.03</td>
</tr>
<tr>
<td>ωB97XD</td>
<td></td>
<td>5.17</td>
</tr>
<tr>
<td>B97D3</td>
<td></td>
<td>5.98</td>
</tr>
<tr>
<td>PBE-D3</td>
<td></td>
<td>6.32</td>
</tr>
<tr>
<td>TPSS-D3</td>
<td></td>
<td>5.50</td>
</tr>
<tr>
<td>M06-L-D3</td>
<td></td>
<td>2.02</td>
</tr>
<tr>
<td>B3LYP-D3</td>
<td></td>
<td>5.15</td>
</tr>
</tbody>
</table>

$^a$The aug-cc-pVDZ basis set was employed in all calculations unless otherwise specified. c.n. denotes coordination number.
Optimized Geometries and Absolute Energies Obtained at the MP2/aug-cc-pVDZ Level of Theory

$\text{VO}_2^+$
Absolute Energy = -1093.236200 Hartrees
Cartesian Coordinates
V  0.0000  0.0000  0.4169
O  0.0000  1.2479  -0.5994
O  0.0000 -1.2479  -0.5994

$\text{VO}_2(\text{H}_2\text{O})^+$
Absolute Energy = -1322.251842 Hartrees
Cartesian Coordinates
V  0.9128  -0.2490  -2.6596
O  1.0976  1.1110  -1.6697
O  0.3804  -1.4041  -1.5435
O -1.0200  0.2633  -3.4321
H -1.7418 -0.3186  -3.1468
H -1.3199  1.1614  -3.2214
O  2.9741  -0.8371  -2.6660
H  3.1632  -1.6701  -2.2063
H  3.5853 -0.1901  -2.2802
O  1.2600 -0.4533  -4.7634
H  0.6120  -0.3039  -5.4668
H  2.0933  -0.7117  -5.1828

$\text{H}_2\text{VO}_3(\text{H}_2\text{O})^+$
Absolute Energy = -1322.218646 Hartrees
Cartesian Coordinates
V  2.0964  1.4268  0.8837
O  0.9126  2.2224  1.9232
O  1.4237  1.1868 -0.5742
O  3.5550  2.6244  0.2892
H  3.7139  2.9152 -0.6698
H  0.0277  2.5616  1.6993
O  3.7736  3.2285 -2.1682
H  4.4759  2.8811 -2.7372
H  3.5601  4.1060 -2.5176
O  2.6675 -0.1254  1.4998
H  4.2200  3.0163  0.8749
H  2.6848 -0.9931  1.0582

$\text{H}_2\text{VO}_4(\text{H}_2\text{O})^+$
Absolute Energy = -1322.166880 Hartrees
Cartesian Coordinates
V  0.2769  0.7656 -0.9472
O -0.9595  0.9964  2.1769
O  0.0584 -0.6376 -0.1056
O  0.1799 -2.9404  0.6734
H  1.0681  3.3237  0.5448
H -1.6165  0.3852 -2.5526
O  0.2475  2.1818  0.0973
H  0.2857  2.2621  1.0660
O  1.8848  0.5272 -1.6773
H -0.0845 -3.0626  1.6045
H  2.2328  1.2477 -2.2388
H  0.1327 -1.8927  0.3552

$\text{VO}_2(\text{AO})(\text{H}_2\text{O})_3^+$
Absolute Energy = -1546.562308 Hartrees
Cartesian Coordinates
V  0.1324  1.0252 -0.4016
O  -0.5392  1.0493 -1.9465
O  -0.8109 -0.8847  2.7738
O  -1.6651  0.3958  0.5191
N   2.2334 -0.7161  0.9561
N   2.1653  0.8959 -0.9561
H   2.7120  1.4392 -1.6198
O   0.0763  2.6251  0.0840
H  -0.6663 -0.2906  3.5218
H   0.0097 -0.8182  2.2286
H   3.9223 -0.2286 -0.4625
H   2.5784 -1.6144  0.9632
O   0.8746 -0.5209  0.7497
H  -2.1129 -0.2092 -0.1126
H  -1.5319 -0.0966  1.3639
O  -2.5302 -0.9602 -1.7097
H  -1.8887 -0.4097 -2.1954
H  -3.3848 -0.7529 -2.1099

$\text{H}_2\text{VO}_3(\text{AO})(\text{H}_2\text{O})_2^+$

Absolute Energy = -1546.539677 Hartrees
Cartesian Coordinates
V   1.4532 -1.8187  0.3581
O   1.9410 -0.1711  0.9352
O   1.4508 -1.4682 -1.2535
C  -1.0003 -2.5549  1.6917
N  -0.5267 -2.2037  0.4939
H  -1.2482 -2.0833 -0.2133
N  -0.1168 -2.7343  2.6557
O   1.1863 -2.5548  2.3650
O   1.8879 -2.2564  4.9041
H   1.9525 -0.4692  4.3057
H   1.8561 -2.4770  3.9407
O   2.8299 -3.0582  0.2319
H   2.9149 -3.4388  1.1250
H   2.6386 -2.7476  5.2606
O   1.8009  0.2749  3.6907
H   2.3699  0.9887  4.0037
H   1.9385 -0.1452  1.9264
H  -2.0548 -2.7122  1.9336
H  -0.3546 -2.9847  3.6138

Complex 1
Absolute Energy = -1398.545356 Hartrees
Cartesian Coordinates
O   0.3604 -2.6448 -0.7723
O  -1.5204 -3.6351  0.7574
O  -1.9947 -3.8756 -1.9453
O   0.8976 -4.9453  0.9184
O  -1.1631 -6.3140 -0.6033
O   0.7302 -5.1600 -2.0823
V  -0.4627 -4.1004 -0.4843
H   0.6016 -6.0947 -2.3027
H   1.4267 -4.8203 -2.6605
H   0.8333 -4.5267  1.7918
H   1.8381 -4.9171  0.6822
H  -2.6714 -3.2356 -1.6721
H  -1.0404 -6.8271  0.2097
Complex 2
Absolute Energy = -1398.541208 Hartrees
Cartesian Coordinates
O    0.2344  -4.0508   1.2520
O   -1.9503  -3.4037  -0.0313
O    0.4409  -2.3565  -1.1153
O   -1.1524  -6.1414  -0.1739
O    0.3930  -4.9437  -2.0790
V   -0.4368  -4.1142  -0.2962
H    0.2818  -5.8616  -2.3607
H    1.0119  -4.4966  -2.6917
H   -2.1205  -6.2032  -0.1656
H   -0.8634  -6.6209   0.6178
H    0.6336  -1.6202  -0.5191
H    1.1733  -2.4132  -1.7597
O   -1.1028  -3.1105  -3.2573
H    1.8573  -2.6801  -4.1008
H    3.0298  -3.2165  -3.2700

Complex 3
Absolute Energy = -1358.697173 Hartrees
Cartesian Coordinates
V    0.1482  -0.3605   0.2816
O    0.4640   0.7467   1.5104
O    1.0607   0.2100  -1.0092
O   -1.7674   0.3620  -0.3385
C    0.0691  -2.7459   0.7624
O    1.1530  -2.0972   0.9161
O   -1.0028  -2.1641   0.3548
H   -2.2730  -0.4602  -0.4581
H   -1.7442   0.7910  -1.2058
H    0.0457  -3.8266   0.9827

Complex 4
Absolute Energy = -1358.682407 sHartrees
Cartesian Coordinates
V   -1.0412   0.6254   0.5267
O   -1.6884   1.0175   2.0104
O   -1.3013  -1.3900   0.2864
O   -2.0086   1.4156  -0.5714
O    0.9345   0.6732   0.2769
O    1.1585  -1.5272  -0.2595
C    1.6246  -0.3651  -0.0807
H   -0.3203  -1.6202   0.0540
H   -1.5322  -1.8788   1.0894
H    2.7015 -0.1728  -0.2316

Complex 5
Absolute Energy = -1434.979157 Hartrees
Cartesian Coordinates
V    2.2016   9.6200  12.1816
O    0.4678   8.5264  12.6333
O    1.5059   9.7164  14.2020
O    3.7651  10.7849  12.9994
O    3.7483  12.6687  11.0781
O    1.7460  10.6456  10.9409
O    3.1425   8.4530  11.4161
Complex 6
Absolute Energy = -1434.981796 Hartrees
Cartesian Coordinates
V  2.2164  9.6024  12.2670
O  0.3634  8.6425  12.6844
O  1.3847  9.8438  14.2491
O  3.7834 10.8521  12.9654
O  1.8526 10.4634  10.8717
O  3.1369  8.3206  11.6976
C  0.3996  9.1079  13.8608
H -0.4175  8.8863  14.5682
H  3.6110 11.1868  13.8858
H  3.8677 11.6350  12.4086
H  2.2907 10.9979  15.3898
O  3.0493 11.6139  15.4242
H  3.5478 11.3691  16.2144

Complex 7
Absolute Energy = -1434.982087 Hartrees
Cartesian Coordinates
V -1.2912  0.5534  0.5708
O -1.1993 -1.5364  0.2383
O  0.7501  0.5665  0.1775
O  1.3540 -1.6036 -0.1432
C  1.6036 -0.3819 -0.0702
H -0.2161 -1.7266  0.0945
H -1.4671 -2.0428  1.0165
H  2.6437 -0.0377 -0.2274
O -0.6303  2.6056  0.8077
H  0.2840  2.4682  0.4936
H -1.0474  3.2018  0.1702
O -2.5339  0.8852 -0.5117
O -2.1046  0.4697  2.0459

Complex 8
Absolute Energy = -1434.978050 Hartrees
Cartesian Coordinates
V  2.6312  9.6650  12.0025
O  0.5409  9.6862  12.1563
O  1.6660 10.5968  13.8643
O  4.4977 10.4210  12.7276
O  2.5302 12.0248  11.6760
O  2.9527  9.5354  10.3426
O  2.8957  8.0757  12.5356
C  0.5798 10.2032  13.3287
H -0.3718 10.3051  13.8820
H  2.1980 12.1261  10.7719
H  1.8172 12.3133  12.2661
H  4.5076 10.2475  13.6823
H  4.3773 11.3823  12.6435

Complex 9
Absolute Energy = -1393.999430 Hartrees
Cartesian Coordinates
V  0.0922  1.0227 -0.4501
O -0.6263  1.0165 -1.9751
O -1.6361  0.2584  0.5978
N  2.0705 -0.8641  0.4704
H  2.7301  1.4888 -1.5272
O  0.3472  2.6243  0.0567
H  3.8400 -0.2873 -0.4305
H  2.4624 -1.6265  1.0106
O  0.7396 -0.6035  0.6264
H -2.2598 -0.0708 -0.0658
H -1.2324 -0.5367  0.9929

Complex 10
Absolute Energy = -1393.984783 Hartrees
Cartesian Coordinates
V -2.1842 -1.1767  0.1110
O -3.1290 -2.2611 -0.7429
O -2.2679 -0.8376  1.9813
O -1.8981  0.1089 -0.9239
O  0.3097 -1.6836  1.4804
N -0.3317 -2.1122  0.2945
C  0.4157 -2.9114 -0.4007
N  1.6695 -3.2785 -0.0423
H  2.0133 -3.0013  0.8693
H  2.1466 -4.0049 -0.5544
H -2.8144 -1.3836  2.5642
H -0.4585 -1.3033  1.9776
H -0.0000 -3.2716 -1.3423

Complex 11
Absolute Energy = -1393.983631 Hartrees
Cartesian Coordinates
V  0.2862 -0.0973 -0.1309
O  0.9661  1.3911 -0.4753
O -0.0426  0.3226  1.9472
O -1.3259  0.0123 -0.5605
O  1.1909 -1.5301 -1.1350
N  1.3115 -1.8502  0.2160
C  1.9464 -3.2498  0.4807
N  0.6914 -3.4528  0.6823

Complex 12
Absolute Energy = -1393.989084 Hartrees
Cartesian Coordinates
V -0.3341  0.3614 -0.9335
O -0.2779  0.5638 -2.6056
O -1.7827  1.0569 -0.4146
O  0.8691 -0.8493  0.1496
N -0.1855 -1.5742 -0.3988
C -0.2205 -2.8434 -0.1482
N  0.6914 -3.4528  0.6823
Complex 13
Absolute Energy = -1393.988844 Hartrees
Cartesian Coordinates
V     0.0559   1.0320  -0.4447
O    -0.6036   1.0557  -2.0034
O    -1.6414  -0.2373   0.5935
N     2.0612  -0.8921   0.5127
C     2.7652  -0.1273  -0.2621
O    -0.0082   2.6337   0.0918
H     3.8332  -0.3292  -0.3633
O     0.7366  -0.5578   0.5675
H    -2.2729  -0.1383  -0.0372
H    -1.1761  -0.5268   0.9919
N     2.1443   0.9746  -0.9863
H     2.5985   1.8617  -0.7560
H     2.2436   0.8454  -1.9964
Complex 14
Absolute Energy = -1393.970530 Hartrees
Cartesian Coordinates
V    -0.0489   0.9050  -0.1102
O    -0.2718   1.3873  -1.7150
O    -1.5886  -0.5829  -0.1615
N     0.9841  -0.8183   0.7460
C     2.0365  -0.3395   0.0524
N     2.0694   1.0022   0.0314
H     2.8261   1.3784  -0.5282
O    -0.8177   2.0792   0.8041
H     2.7308  -1.0180  -0.4668
O     0.6823  -2.1905   0.3622
H    -1.0956  -1.4024   0.0579
H    -2.1899  -0.4293   0.5821
H     0.7131  -2.6565   1.2137
Complex 15
Absolute Energy = -1393.972482 Hartrees
Cartesian Coordinates
V    -0.1737   0.8829  -0.1771
O    -0.3814   1.5320  -1.7189
O    -1.6384  -0.6264  -0.0436
N     0.8732  -0.8873   0.3365
C     2.1003  -0.4172   0.3810
N     2.0164   1.0022   0.0469
H     2.5230   1.2464  -0.8058
O    -0.7026   2.0599   0.9095
H     3.0228  -0.9529   0.6254
O     0.4408  -2.0705   0.5690
H    -1.0684  -1.4160   0.2485
H    -2.3144  -0.4967   0.6354
H     2.3411   1.6114   0.7996
Complex 16
Absolute Energy = -1470.282922 Hartrees
### Cartesian Coordinates

<table>
<thead>
<tr>
<th>Complex</th>
<th>Absolute Energy</th>
<th>Cartesian Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex 17</td>
<td>-1470.277878 Ha</td>
<td>V  0.0385    0.9331 -0.3814</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  -0.5396   1.3089 -1.9218</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  -0.7049   -0.3735 2.7246</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  -1.7939   0.0782  0.3027</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N  2.0839    -0.9914  0.4157</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C  2.7652    -0.0914 -0.3016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N  2.1116    0.9397  -0.7847</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H  2.7038    1.6093 -1.2702</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  -0.1307   2.3679  0.4781</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H  -0.4495   0.4620  3.1400</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H  0.0368    -0.5807  2.1056</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H  3.8410    -0.2689 -0.4102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H  2.4319    -1.9296  0.5863</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  0.7161    -0.8360  0.4811</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H  -1.8920   -0.8026 -0.0891</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H  -1.6210   -0.0919  1.2657</td>
</tr>
<tr>
<td>Complex 18</td>
<td>-1470.275822 Ha</td>
<td>V  -2.2756   -1.1028  0.0391</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  -2.9869   -2.3132 -0.8846</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  -2.1521   -0.8215  2.0474</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  -1.7294   0.0169 -1.0848</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  -4.0824   -0.0048  0.5571</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O  0.2414    -1.6793  1.5457</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N  -0.4106   -2.0890  0.3716</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C  0.3032    -2.9119 -0.3271</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N  1.5237    -3.3849  0.0631</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H  1.9736    -2.9077  0.8364</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H  2.1159    -3.8125 -0.6345</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H  -2.5199   -1.5300  2.5977</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H  -0.5323   -1.2255  1.9977</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H  -0.1318   -3.2654 -1.2627</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H  -3.6838   0.1353  1.4462</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H  -4.0926   0.8590  0.1209</td>
</tr>
</tbody>
</table>

### Complex 17
Absolute Energy = -1470.277878 Hartrees

### Complex 18
Absolute Energy = -1470.275822 Hartrees
Complex 19
Absolute Energy = -1470.275291 Hartrees
Cartesian Coordinates
V  0.0922  1.0434 -0.4524
O -0.6022  0.7590 -1.9654
O -0.9112 -1.1538  2.4887
O -1.6669  0.6018  0.6571
N  2.2736 -0.4882  0.8450
C  2.8874  2.7176 -0.2862
H -0.3085 -0.8894  3.4119
H -0.0288 -0.9828  2.0639
H  3.9652 -0.0695 -0.2381
O  0.9221 -0.2477  0.8709
H -2.3268  0.1867  0.0856
H -1.5102 -0.0388 -1.1143
N  2.5807  1.7957 -1.2256
H  2.1712  0.4270 -2.0351

Complex 20
Absolute Energy = -1470.262919 Hartrees
Cartesian Coordinates
V  0.4284  0.5952 -0.3818
O  0.9263  1.0703 -1.9171
O  0.2976  0.3788  1.9355
O  0.7845  2.5189  0.4548
O -1.2161  0.3618 -0.5399
O  1.5061 -1.0144 -0.2559
N  1.2648 -1.7769  0.9005
C  1.6689 -3.0055  0.7439
N  2.2871 -3.4702 -0.3900
H  2.1942 -2.8544 -1.1938
H  2.2561 -4.4658 -0.5653
H -0.6527  0.1922  1.9888
H  0.6997 -0.5459  1.8624
H  0.3686  3.2921  0.0510
H  0.4975  2.4683  1.3810
H  1.5530 -3.6799  1.5946

Complex 21
Absolute Energy = -1546.562308 Hartrees
Cartesian Coordinates
V  0.1324  1.0252 -0.4016
O -0.5392  1.0493 -1.9465
O -0.8109 -0.8847  2.7738
O -1.6651  0.3958  0.5191
N  2.2334 -0.7161  0.6384
C  2.8588 -0.0133 -0.3119
N  2.1653  0.8959 -0.9561
H  2.7120  1.4392 -1.6198
O  0.0763  2.6251  0.0840
H -0.6663 -0.2906  3.5218
H  0.0097 -0.8182  2.2286
H  3.9233 -0.2286 -0.4625
H  2.5784 -1.6144  0.9632
O  0.8746 -0.5209  0.7497
H -2.1129 -0.2092 -0.1126
Complex 22
Absolute Energy = -1546.563673 Hartrees
Cartesian Coordinates

Complex 23
Absolute Energy = -1546.556854 Hartrees
Cartesian Coordinates

Complex 24
Absolute Energy = -1546.554129 Hartrees
Cartesian Coordinates
<table>
<thead>
<tr>
<th>Symbol</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3.0149</td>
<td>0.1889</td>
<td>-0.0239</td>
</tr>
<tr>
<td>O</td>
<td>0.0587</td>
<td>2.5902</td>
<td>-0.4098</td>
</tr>
<tr>
<td>H</td>
<td>-0.7708</td>
<td>-0.8836</td>
<td>3.4268</td>
</tr>
<tr>
<td>H</td>
<td>0.0726</td>
<td>-0.9911</td>
<td>-0.0611</td>
</tr>
<tr>
<td>O</td>
<td>1.0320</td>
<td>-0.2242</td>
<td>0.9186</td>
</tr>
<tr>
<td>H</td>
<td>-2.1880</td>
<td>-0.0604</td>
<td>-0.0954</td>
</tr>
<tr>
<td>H</td>
<td>-1.4422</td>
<td>-1.926</td>
<td>1.3060</td>
</tr>
<tr>
<td>O</td>
<td>-2.9380</td>
<td>-0.6925</td>
<td>-1.5996</td>
</tr>
<tr>
<td>H</td>
<td>-2.2267</td>
<td>-0.4070</td>
<td>-2.1987</td>
</tr>
<tr>
<td>H</td>
<td>-3.7289</td>
<td>-0.2427</td>
<td>-1.9252</td>
</tr>
<tr>
<td>N</td>
<td>2.2663</td>
<td>0.8591</td>
<td>-1.0720</td>
</tr>
<tr>
<td>Complex 25</td>
<td>Absolute Energy = -1546.549250 Hartrees</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>-0.3424</td>
<td>0.5467</td>
<td>-0.3443</td>
</tr>
<tr>
<td>O</td>
<td>-0.2937</td>
<td>0.5714</td>
<td>-2.0364</td>
</tr>
<tr>
<td>O</td>
<td>-0.2222</td>
<td>0.6725</td>
<td>2.0502</td>
</tr>
<tr>
<td>O</td>
<td>-1.9321</td>
<td>1.0415</td>
<td>-0.0244</td>
</tr>
<tr>
<td>O</td>
<td>1.3515</td>
<td>-0.7284</td>
<td>0.0978</td>
</tr>
<tr>
<td>N</td>
<td>0.1411</td>
<td>-1.3956</td>
<td>0.0314</td>
</tr>
<tr>
<td>C</td>
<td>0.1627</td>
<td>-2.6787</td>
<td>0.2070</td>
</tr>
<tr>
<td>N</td>
<td>1.3207</td>
<td>-3.3542</td>
<td>0.5354</td>
</tr>
<tr>
<td>H</td>
<td>2.1579</td>
<td>-2.8170</td>
<td>0.3163</td>
</tr>
<tr>
<td>H</td>
<td>1.3530</td>
<td>-4.3308</td>
<td>0.2668</td>
</tr>
<tr>
<td>O</td>
<td>0.8374</td>
<td>2.3109</td>
<td>-0.0988</td>
</tr>
<tr>
<td>H</td>
<td>-0.9685</td>
<td>1.2530</td>
<td>2.2553</td>
</tr>
<tr>
<td>H</td>
<td>0.5614</td>
<td>1.0513</td>
<td>2.4809</td>
</tr>
<tr>
<td>H</td>
<td>-0.7829</td>
<td>-3.2179</td>
<td>0.1460</td>
</tr>
<tr>
<td>H</td>
<td>1.2409</td>
<td>2.5135</td>
<td>0.9549</td>
</tr>
<tr>
<td>H</td>
<td>1.5798</td>
<td>2.0221</td>
<td>0.4887</td>
</tr>
<tr>
<td>O</td>
<td>2.4336</td>
<td>1.0231</td>
<td>1.6800</td>
</tr>
<tr>
<td>H</td>
<td>3.3783</td>
<td>0.9009</td>
<td>1.8324</td>
</tr>
<tr>
<td>H</td>
<td>2.1021</td>
<td>0.1880</td>
<td>1.2380</td>
</tr>
<tr>
<td>Complex S1</td>
<td>Absolute Energy = -1511.261465 Hartrees</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>2.1353</td>
<td>9.6790</td>
<td>12.2772</td>
</tr>
<tr>
<td>O</td>
<td>0.3723</td>
<td>8.5914</td>
<td>12.7249</td>
</tr>
<tr>
<td>O</td>
<td>1.4332</td>
<td>9.7085</td>
<td>14.3236</td>
</tr>
<tr>
<td>O</td>
<td>3.8002</td>
<td>10.7254</td>
<td>13.0077</td>
</tr>
<tr>
<td>O</td>
<td>3.9885</td>
<td>12.3891</td>
<td>10.8491</td>
</tr>
<tr>
<td>O</td>
<td>1.6300</td>
<td>10.7481</td>
<td>11.0997</td>
</tr>
<tr>
<td>O</td>
<td>2.9800</td>
<td>8.5112</td>
<td>11.4086</td>
</tr>
<tr>
<td>O</td>
<td>0.4584</td>
<td>8.9645</td>
<td>13.9337</td>
</tr>
<tr>
<td>C</td>
<td>-0.3067</td>
<td>8.6484</td>
<td>14.6630</td>
</tr>
<tr>
<td>H</td>
<td>3.1327</td>
<td>12.1160</td>
<td>10.4784</td>
</tr>
<tr>
<td>H</td>
<td>3.9716</td>
<td>13.3549</td>
<td>10.8315</td>
</tr>
<tr>
<td>H</td>
<td>3.5803</td>
<td>11.1827</td>
<td>13.8556</td>
</tr>
<tr>
<td>H</td>
<td>4.0038</td>
<td>11.4273</td>
<td>12.3477</td>
</tr>
<tr>
<td>H</td>
<td>2.2283</td>
<td>11.0522</td>
<td>15.3787</td>
</tr>
<tr>
<td>O</td>
<td>2.9070</td>
<td>11.7541</td>
<td>15.3651</td>
</tr>
<tr>
<td>H</td>
<td>3.4020</td>
<td>11.6476</td>
<td>16.1874</td>
</tr>
</tbody>
</table>
Complex S2
Absolute Energy = -1511.262636 Hartrees
Cartesian Coordinates
V  -1.2331  0.4792  0.6384
O  -1.1165 -1.6140  0.3712
O   0.7906  0.4839  0.2037
O  1.3943 -1.6806 -0.1608
C  1.6367 -0.4554 -0.0874
H  -0.1406 -1.7997  0.1624
H  -1.3257 -2.1055  1.1764
H   2.6673 -0.1039 -0.2852
O  -0.6414  2.5245  0.8742
H   0.2639  2.4818  0.5210
H  -1.1673  3.0553  0.2305
O  -2.4434  0.7830 -0.4732
O  -2.0742  0.3926  2.0956
O  -2.2899  3.5771 -1.0253
H  -2.7492  2.7412 -1.2121
H  -2.9931  4.2138 -0.8416

Complex S3
Absolute Energy = -1511.263902 Hartrees
Cartesian Coordinates
V  -0.4585  0.5784 -0.3167
O  -0.3108  0.5745 -2.0087
O  -0.2472  0.6006  1.9880
O  -1.9906  1.2798 -0.1217
O   1.3500 -0.7847  0.1684
C   0.4676 -1.7112  0.1933
O   0.7869  2.3171 -0.0615
H  -0.9215  1.2115  2.3166
H   0.6057  0.9089  2.3394
H  1.1399  2.5778 -0.9235
H   1.5638  2.0392  0.4780
O   2.4929  1.0540  1.6431
H   3.4136  1.0612  1.9309
H   2.3418  0.1957  1.1791
O  -0.7589 -1.4868 -0.0554
H   0.7770 -2.7469  0.4215

Optimized Geometries and Absolute Energies Obtained at the B3LYP/aug-cc-pVDZ Level of Theory
VO₂⁺
Absolute Energy = -1094.198446 Hartrees
Cartesian Coordinates
V  0.010592  0.000000  0.008000
O  0.009996  0.000000  1.558220
O  1.501554  0.000000 -0.416515

Complex 1
Absolute Energy = -1400.211579 Hartrees
Cartesian Coordinates
O   0.379485 -2.745090 -0.830609
O  -1.465735 -3.640096  0.701711
O  -1.953706 -3.900414 -1.955501
O   0.901174 -4.956031  0.870030
O  -1.191209 -6.278038 -0.561911
O   0.713230 -5.143943 -2.056998
V  -0.461233 -4.039570 -0.463068

S13
Complex 2
Absolute Energy = -1400.217767 Hartrees
Cartesian Coordinates

Complex 3
Absolute Energy = -1360.301270 Hartrees
Cartesian Coordinates

Complex 4
Absolute Energy = -1360.301193 Hartrees
Cartesian Coordinates

Complex 5
Absolute Energy = -1436.768243 Hartrees
Cartesian Coordinates
Complex 6
Absolute Energy = -1436.766267 Hartrees
Cartesian Coordinates
V  2.241368  9.558049  12.212201
O  0.407852  8.716718  12.638706
O  1.382091  9.857572  14.220952
O  3.601423 10.939215  12.942459
O  1.958359 10.341864  10.851816
O  3.165701  8.297919  11.930235
C  0.398429  9.156028  13.822739
H  0.447762  8.933291  14.492037
H  3.530405 11.236085  13.894177
H  3.699172 11.712395  12.373596
H  2.351715 10.952661  15.463990
H  3.123058 11.549714  15.453282
H  3.694189 11.270189  16.184864

Complex 7
Absolute Energy = -1436.767201 Hartrees
Cartesian Coordinates
V  -1.284791  0.532032  0.575229
O  -1.166014 -1.490446  0.226392
O   0.710811  0.524946  0.149055
O  1.337297 -1.632058 -0.066065
C  1.576923 -0.416797 -0.040482
H  -0.179355 -1.746373  0.122135
H  -1.566997 -2.021562  0.925450
H  2.614262 -0.066780 -0.191993
O  -0.626585  2.580570  0.775267
O  -0.626585  2.605160  0.371471
O  -1.201568  3.167871  0.265553
O  -2.402671  0.955315 -0.483907
O  -1.921308  0.433376  2.034295

Four-Coordinate VO₂(HCOO)(H₂O) Complex
Absolute Energy = -1436.766288 Hartrees
Cartesian Coordinates
V  1.751693  8.720614  12.577831
O  1.622167  9.668291  14.158649
O  3.717094 10.778897  12.931635
O  3.687434 12.688349  11.137987
O  1.897841 10.605477  10.913050
O  3.110899  8.367745  11.543760
C  0.584088  9.031944  13.801891
H  -0.193059  8.751569  14.530519
H  2.968394 12.181882  10.707529
H  3.374029 13.597503  11.209815
H  3.813220 11.626252  12.407698
H  3.533441 10.989068  13.857262

S15
<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2.966525</td>
<td>11.004509</td>
<td>12.210350</td>
</tr>
<tr>
<td>H</td>
<td>4.306469</td>
<td>9.659910</td>
<td>15.419131</td>
</tr>
<tr>
<td>O</td>
<td>3.546782</td>
<td>10.141523</td>
<td>15.069702</td>
</tr>
<tr>
<td>H</td>
<td>2.730187</td>
<td>9.663435</td>
<td>15.384207</td>
</tr>
</tbody>
</table>

**Complex 9**
Absolute Energy = -1395.740582 Hartrees
Cartesian Coordinates

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>0.115968</td>
<td>1.052107</td>
<td>-0.444132</td>
</tr>
<tr>
<td>O</td>
<td>-0.604067</td>
<td>0.964757</td>
<td>-1.880703</td>
</tr>
<tr>
<td>O</td>
<td>-1.608485</td>
<td>0.229875</td>
<td>0.560467</td>
</tr>
<tr>
<td>N</td>
<td>2.084562</td>
<td>-0.827141</td>
<td>0.499025</td>
</tr>
<tr>
<td>C</td>
<td>2.769797</td>
<td>-0.060840</td>
<td>-0.332825</td>
</tr>
<tr>
<td>N</td>
<td>2.104342</td>
<td>0.891860</td>
<td>-0.941320</td>
</tr>
<tr>
<td>H</td>
<td>2.631721</td>
<td>1.474661</td>
<td>-1.578549</td>
</tr>
<tr>
<td>O</td>
<td>0.045996</td>
<td>2.544863</td>
<td>0.126251</td>
</tr>
<tr>
<td>H</td>
<td>3.833844</td>
<td>-0.268446</td>
<td>-0.460632</td>
</tr>
<tr>
<td>H</td>
<td>2.465404</td>
<td>-1.582723</td>
<td>1.051419</td>
</tr>
<tr>
<td>O</td>
<td>0.758724</td>
<td>-0.553021</td>
<td>0.642584</td>
</tr>
<tr>
<td>H</td>
<td>-2.258111</td>
<td>0.026226</td>
<td>-0.126751</td>
</tr>
<tr>
<td>H</td>
<td>-1.306995</td>
<td>-0.614177</td>
<td>0.933566</td>
</tr>
</tbody>
</table>

**Complex 10**
Absolute Energy = -1395.741404 Hartrees
Cartesian Coordinates

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>-2.136784</td>
<td>-1.189736</td>
<td>0.070467</td>
</tr>
<tr>
<td>O</td>
<td>-3.099718</td>
<td>-2.264446</td>
<td>-0.627765</td>
</tr>
<tr>
<td>O</td>
<td>-2.349950</td>
<td>-0.831977</td>
<td>1.866563</td>
</tr>
<tr>
<td>O</td>
<td>-1.918682</td>
<td>0.104668</td>
<td>-0.845542</td>
</tr>
<tr>
<td>O</td>
<td>0.360890</td>
<td>-1.691129</td>
<td>1.527913</td>
</tr>
<tr>
<td>N</td>
<td>-0.302879</td>
<td>-2.103762</td>
<td>0.360249</td>
</tr>
<tr>
<td>C</td>
<td>0.406740</td>
<td>-2.911739</td>
<td>-0.361308</td>
</tr>
<tr>
<td>N</td>
<td>1.639981</td>
<td>-3.335341</td>
<td>-0.041753</td>
</tr>
<tr>
<td>H</td>
<td>2.078133</td>
<td>-3.012441</td>
<td>0.809317</td>
</tr>
<tr>
<td>H</td>
<td>2.135162</td>
<td>-3.972043</td>
<td>-0.643886</td>
</tr>
<tr>
<td>H</td>
<td>-2.939007</td>
<td>-1.379555</td>
<td>2.400433</td>
</tr>
<tr>
<td>H</td>
<td>-0.356936</td>
<td>-1.271306</td>
<td>2.045314</td>
</tr>
<tr>
<td>H</td>
<td>-0.046050</td>
<td>-3.258194</td>
<td>-1.288302</td>
</tr>
</tbody>
</table>

**Complex 11**
Absolute Energy = -1395.733252 Hartrees
Cartesian Coordinates

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>0.055457</td>
<td>1.049748</td>
<td>-0.432735</td>
</tr>
<tr>
<td>O</td>
<td>-0.538727</td>
<td>0.977084</td>
<td>-1.928280</td>
</tr>
<tr>
<td>O</td>
<td>-1.631024</td>
<td>0.218438</td>
<td>0.562479</td>
</tr>
<tr>
<td>N</td>
<td>2.064827</td>
<td>-0.842180</td>
<td>0.513937</td>
</tr>
<tr>
<td>C</td>
<td>2.768772</td>
<td>-0.111460</td>
<td>-0.261708</td>
</tr>
<tr>
<td>O</td>
<td>0.113181</td>
<td>2.549166</td>
<td>0.133138</td>
</tr>
<tr>
<td>H</td>
<td>3.834397</td>
<td>-0.303449</td>
<td>-0.371151</td>
</tr>
<tr>
<td>O</td>
<td>0.752346</td>
<td>-0.502250</td>
<td>0.555846</td>
</tr>
<tr>
<td>H</td>
<td>-2.307673</td>
<td>-0.068462</td>
<td>-0.066005</td>
</tr>
<tr>
<td>H</td>
<td>-1.260734</td>
<td>-0.578339</td>
<td>0.983246</td>
</tr>
<tr>
<td>N</td>
<td>2.130457</td>
<td>0.970729</td>
<td>-0.994829</td>
</tr>
<tr>
<td>H</td>
<td>2.554992</td>
<td>1.874111</td>
<td>-0.781496</td>
</tr>
<tr>
<td>H</td>
<td>2.199829</td>
<td>0.835863</td>
<td>-2.004539</td>
</tr>
</tbody>
</table>

**Complex 12**
Absolute Energy = -1395.733252 Hartrees
Cartesian Coordinates

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>-0.345890</td>
<td>0.339344</td>
<td>-0.939562</td>
</tr>
<tr>
<td>Atom</td>
<td>X</td>
<td>Y</td>
<td>Z</td>
</tr>
<tr>
<td>------</td>
<td>------------</td>
<td>------------</td>
<td>------------</td>
</tr>
<tr>
<td>O</td>
<td>-0.254246</td>
<td>0.474853</td>
<td>-2.532130</td>
</tr>
<tr>
<td>O</td>
<td>-1.687847</td>
<td>0.995296</td>
<td>-0.339476</td>
</tr>
<tr>
<td>O</td>
<td>0.895931</td>
<td>-0.803697</td>
<td>0.121334</td>
</tr>
<tr>
<td>N</td>
<td>-0.150061</td>
<td>-1.543359</td>
<td>-0.378786</td>
</tr>
<tr>
<td>C</td>
<td>-0.206557</td>
<td>-3.473266</td>
<td>0.597104</td>
</tr>
<tr>
<td>H</td>
<td>1.547222</td>
<td>-2.975039</td>
<td>0.854562</td>
</tr>
<tr>
<td>H</td>
<td>0.737507</td>
<td>-4.479479</td>
<td>0.565392</td>
</tr>
<tr>
<td>O</td>
<td>0.958156</td>
<td>1.870147</td>
<td>-0.267264</td>
</tr>
<tr>
<td>H</td>
<td>-1.047849</td>
<td>-3.356534</td>
<td>-0.267264</td>
</tr>
<tr>
<td>H</td>
<td>0.428287</td>
<td>2.585964</td>
<td>0.112129</td>
</tr>
<tr>
<td>H</td>
<td>1.496375</td>
<td>1.502332</td>
<td>0.449371</td>
</tr>
</tbody>
</table>

**Complex 13**

Absolute Energy = -1395.727057 Hartrees

Cartesian Coordinates

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>0.2935</td>
<td>0.3275</td>
<td>-0.4283</td>
</tr>
<tr>
<td>O</td>
<td>0.7283</td>
<td>1.5664</td>
<td>-1.3326</td>
</tr>
<tr>
<td>O</td>
<td>0.3787</td>
<td>0.5041</td>
<td>1.6239</td>
</tr>
<tr>
<td>O</td>
<td>-1.2027</td>
<td>-0.1438</td>
<td>-0.7583</td>
</tr>
<tr>
<td>O</td>
<td>1.5853</td>
<td>-1.0163</td>
<td>-0.3021</td>
</tr>
<tr>
<td>N</td>
<td>1.2904</td>
<td>-1.7748</td>
<td>0.8525</td>
</tr>
<tr>
<td>C</td>
<td>1.6182</td>
<td>-3.0193</td>
<td>0.7155</td>
</tr>
<tr>
<td>N</td>
<td>2.1500</td>
<td>-3.5681</td>
<td>-0.3972</td>
</tr>
<tr>
<td>H</td>
<td>2.2783</td>
<td>-2.9850</td>
<td>-1.2123</td>
</tr>
<tr>
<td>H</td>
<td>2.3497</td>
<td>-4.5526</td>
<td>-0.4475</td>
</tr>
<tr>
<td>H</td>
<td>-0.4673</td>
<td>0.5985</td>
<td>2.0819</td>
</tr>
<tr>
<td>H</td>
<td>0.7023</td>
<td>-0.4515</td>
<td>1.7578</td>
</tr>
<tr>
<td>H</td>
<td>1.4589</td>
<td>-3.6640</td>
<td>1.5793</td>
</tr>
</tbody>
</table>

**Complex 14**

Absolute Energy = -1395.704388 Hartrees

Cartesian Coordinates

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>-0.045643</td>
<td>0.921272</td>
<td>-0.161637</td>
</tr>
<tr>
<td>O</td>
<td>-0.240843</td>
<td>1.305859</td>
<td>-1.701388</td>
</tr>
<tr>
<td>O</td>
<td>-1.603684</td>
<td>-0.538405</td>
<td>-0.098822</td>
</tr>
<tr>
<td>N</td>
<td>0.977463</td>
<td>-0.845730</td>
<td>0.638759</td>
</tr>
<tr>
<td>C</td>
<td>2.070065</td>
<td>-0.348136</td>
<td>0.055864</td>
</tr>
<tr>
<td>N</td>
<td>2.014160</td>
<td>0.971374</td>
<td>0.007096</td>
</tr>
<tr>
<td>H</td>
<td>2.751012</td>
<td>1.448346</td>
<td>-0.497514</td>
</tr>
<tr>
<td>O</td>
<td>-0.741728</td>
<td>1.997616</td>
<td>0.796100</td>
</tr>
<tr>
<td>H</td>
<td>2.855528</td>
<td>-0.984886</td>
<td>-0.371947</td>
</tr>
<tr>
<td>O</td>
<td>0.733100</td>
<td>-2.221873</td>
<td>0.322890</td>
</tr>
<tr>
<td>H</td>
<td>-1.217371</td>
<td>-1.411945</td>
<td>0.093754</td>
</tr>
<tr>
<td>H</td>
<td>-2.240763</td>
<td>-0.331542</td>
<td>0.598204</td>
</tr>
<tr>
<td>H</td>
<td>0.718402</td>
<td>-2.659451</td>
<td>1.186741</td>
</tr>
</tbody>
</table>

**Complex 15**

Absolute Energy = -1395.709269 Hartrees

Cartesian Coordinates

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>-0.201170</td>
<td>0.892330</td>
<td>-0.182218</td>
</tr>
<tr>
<td>O</td>
<td>-0.283156</td>
<td>1.447956</td>
<td>-1.680005</td>
</tr>
<tr>
<td>O</td>
<td>-1.597082</td>
<td>-0.609665</td>
<td>-0.011577</td>
</tr>
<tr>
<td>N</td>
<td>0.868110</td>
<td>-0.854346</td>
<td>0.327095</td>
</tr>
<tr>
<td>C</td>
<td>2.075221</td>
<td>-0.405679</td>
<td>0.369564</td>
</tr>
<tr>
<td>N</td>
<td>1.997688</td>
<td>1.008913</td>
<td>0.048898</td>
</tr>
<tr>
<td>H</td>
<td>2.477705</td>
<td>1.272706</td>
<td>-0.810719</td>
</tr>
<tr>
<td>O</td>
<td>-0.629114</td>
<td>1.980211</td>
<td>0.914740</td>
</tr>
<tr>
<td>H</td>
<td>2.992428</td>
<td>-0.948223</td>
<td>0.602973</td>
</tr>
</tbody>
</table>
Complex 16
Absolute Energy = -1472.203027 Hartrees
Cartesian Coordinates
V 0.135064 1.052678 -0.483787
O -0.567201 0.890058 -1.920452
O -0.931333 -1.020202 2.639665
O -1.613907 0.440393 0.527825
N 2.232691 -0.642426 0.638105
C 2.827309 -0.028604 -0.377913
N 2.102027 0.806058 -1.071821
H 2.571650 1.301543 -1.818989
O 0.171630 2.592703 -0.056295
H -0.872415 -0.544514 3.476956
H -0.059614 -0.908452 1.194177
H 3.881345 -0.250775 -0.556550
H 2.608832 -1.456587 0.105570
O 0.891227 -0.409674 0.786096
H -2.236049 0.032811 -0.086110
H -1.544157 -0.121709 1.344423

Complex 17
Absolute Energy = -1472.200707 Hartrees
Cartesian Coordinates
V -2.193113 -1.079742 0.130545
O -2.843768 -2.263261 -0.740663
O -2.127662 -0.879946 2.048333
O -1.705161 0.147091 -0.788935
O -4.121065 -0.068127 0.513196
O 0.351736 -1.694721 1.591301
O -0.350066 -2.046706 0.435400
C 0.300466 -2.853799 -0.334610
N 1.534142 -3.331070 -0.071770
H 2.009526 -3.047392 0.772459
H 1.985080 -3.966516 -0.707776
H -2.562341 -1.551350 2.588912
H -0.369113 -1.256389 2.108027
H -0.200750 -3.154746 -1.252024
H -3.904996 0.419708 1.323057
H -4.242514 0.589767 -0.186152

Complex 18
Absolute Energy = -1472.198576 Hartrees
Cartesian Coordinates
V -0.316064 0.326026 -0.845738
O -0.268944 0.471304 -2.440152
O 1.319439 0.935225 2.239345
O -1.682751 0.905429 -0.231917
O 0.892301 -0.888282 0.234737
N -0.163792 -1.581454 -0.316474
C -0.214022 -2.860892 -0.202027
N 0.692942 -3.580704 0.510840
H 1.548130 -3.109569 0.777271
H 0.724406 -4.581073 0.393799
O 1.007275 1.812775 -0.238948
Complex 19
Absolute Energy = -1472.197307 Hartrees
Cartesian Coordinates
V  0.4809  0.5694  -0.9697
O  0.8750  1.1169  -2.4192
O  0.3655  0.4828  2.4567
O  0.7875  1.9983  0.4450
O  -1.0746  0.1877  -0.8894
O  1.6167  -0.7619  -0.3761
N  1.2496  -1.4625  0.7867
C  1.5433  -2.7200  0.6881
N  2.0921  -3.3201  -0.3906
H  2.2935  -2.7632  -1.2090
H  2.2868  -4.3067  -0.3946
H  -0.5619  0.3253  2.6744
H  0.6742  -0.3511  1.9890
H  0.3381  2.8492  0.3750
H  0.5705  1.5580  1.3432
H  1.3268  -3.3378  1.5592

Complex 20
Absolute Energy = -1472.192635 Hartrees
Cartesian Coordinates
V  0.0751  1.0538  -0.4499
O  -0.5058  0.6976  -1.9085
O  -0.9234  -1.0980  2.5194
O  -1.6393  0.5360  0.6170
N  2.2535  -0.5000  0.7872
C  2.8725  0.0603  -0.1783
O  0.1821  2.6361  -0.2210
H  -0.8438  -0.8132  3.4374
H  -0.0355  -0.9667  2.1055
H  3.9430  -0.995  -0.2945
O  0.9182  -0.2294  0.8224
H  -2.3153  0.1601  0.0398
H  -1.5240  -0.0702  1.4095
N  2.1382  0.8946  -1.1069
H  2.5218  1.8386  -1.1573
H  2.1471  0.5117  -2.0531

Complex 21
Absolute Energy = -1548.668264 Hartrees
Cartesian Coordinates
V  0.163038  0.937158  -0.486461
O  -0.483931  0.722657  -1.962446
O  -0.839831  -1.058608  2.730425
O  -1.534546  0.216641  0.451738
N  2.355881  -0.518503  0.769037
C  2.921675  0.053410  -0.284738
N  2.142814  0.770604  -1.050483
H  2.580414  1.236547  -1.835079
O  0.124044  2.481547  -0.094747
H  -0.864432  -0.504997  3.520098
Complex 22
Absolute Energy = -1548.666049 Hartrees
Cartesian Coordinates

Complex 23
Absolute Energy = -1548.664163 Hartrees
Cartesian Coordinates

Complex 24
Absolute Energy = -1548.656813 Hartrees
Cartesian Coordinates
Figure 11, reactant
Absolute Energy = -454.595311445 Hartrees
Cartesian Coordinates
N  -0.8180  -1.5483   0.0757
C  -0.2680  -1.4795  -1.0963
H   0.2683  -2.3811  -1.3967
O  -1.5130  -0.3258   0.3504
N  -0.3102  -0.4497  -1.9733
H  -0.5179   0.4986  -1.6431
H   0.2850  -0.5110  -2.7850
O  -0.2304  -2.3209  -1.0678
H   0.2968  -2.1343  -0.2596
O   1.2991  -1.7224   1.1980
H   2.2234   1.9945   1.1830
H   1.3084   0.7834   1.4855
H  -1.0401   2.7295  -0.7413
H   0.6060  -1.3848   1.3434
O   1.3245  -0.9925   1.8880
H   1.1798  -1.3099   2.7863
H  -1.9858  -0.5317   1.1651
Figure 11, transition state
Absolute Energy = -454.549629140 Hartrees
Cartesian Coordinates
N   2.2915  -0.5455   0.6658
C   2.8815  -0.4352  -0.5225
H   3.6606  -1.1846  -0.6829
O   3.106   0.4317   0.9307
N   2.5875   0.4517  -1.4404
H   2.3530   1.4878  -1.0801
H   3.1431   0.3915  -2.2850
O   2.5970   2.7835  -0.4683
H   3.3523   2.4643   0.2897
O   4.2445   1.9274   1.1332
H   5.0667   2.4275   1.1452
H   4.2547   0.7599   1.9506
H   1.8441   3.1304   0.0238
H   2.9753  -0.6272   1.5035
<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>4.1452</td>
<td>-0.1916</td>
<td>2.4288</td>
</tr>
<tr>
<td>H</td>
<td>3.9968</td>
<td>-0.0245</td>
<td>3.3657</td>
</tr>
<tr>
<td>H</td>
<td>0.5740</td>
<td>-0.0783</td>
<td>1.2966</td>
</tr>
</tbody>
</table>

**Figure 11, product**
Absolute Energy = -454.583306000 Hartrees
Cartesian Coordinates

| N     | -0.7500  | -1.3440  | 0.1420   |
| C     | -0.1067  | -1.2667  | -1.0683  |
| H     | 0.7131   | -1.9988  | -1.1097  |
| O     | -1.6946  | -0.3243  | 0.4017   |
| N     | -0.4450  | -0.4845  | -2.0301  |
| H     | -0.5205  | 1.2725   | -1.3983  |
| H     | 0.1372   | -0.6604  | -2.8478  |
| O     | -0.3508  | 2.1366   | -0.9504  |
| H     | 0.8758   | 1.8152   | 0.2606   |
| O     | 1.5461   | 1.5898   | 0.9529   |
| H     | 2.3727   | 1.9837   | 0.6548   |
| H     | 1.4802   | -0.0053  | 1.7023   |
| H     | -1.1701  | 2.3119   | -0.4716  |
| H     | -0.1208  | -1.4225  | 0.9537   |
| O     | 1.3519   | -0.9252  | 2.0335   |
| H     | 1.3425   | -0.8568  | 2.9944   |
| H     | -2.5498  | -0.7508  | 0.2539   |

**Figure 12, reactant**
Absolute Energy = -1701.56628149 Hartrees
Cartesian Coordinates

| V     | -1.3462  | -0.3894  | -0.6491  |
| O     | -1.9510  | -1.0907  | -1.9582  |
| N     | 0.9005   | -1.7244  | 0.6227   |
| C     | 1.4462   | -1.2163  | -0.4140  |
| O     | -1.6296  | 1.2039   | -0.6279  |
| H     | 2.5040   | -1.3919  | -0.6035  |
| O     | -0.4237  | -1.4174  | 0.7536   |
| N     | 0.6869   | -0.3230  | -1.2480  |
| H     | 1.0798   | 0.6552   | -1.0817  |
| H     | 0.8034   | -0.5375  | -2.2384  |
| O     | 1.8512   | 2.0389   | -0.5964  |
| H     | 2.3684   | 1.8632   | 0.2163   |
| O     | 3.2916   | 1.2385   | 1.6720   |
| H     | 4.2155   | 1.4347   | 1.8583   |
| H     | 3.0869   | 0.4062   | 2.1511   |
| H     | 1.1792   | 2.7160   | -0.3647  |
| H     | 1.9968   | -1.5886  | 2.2088   |
| O     | 2.6299   | -1.2043  | 2.8515   |
| H     | 2.1768   | -1.2180  | 3.7024   |
| O     | -0.3758  | 3.5933   | -0.0354  |
| H     | -0.9682  | 2.8307   | -0.2093  |
| H     | -0.6767  | 4.2933   | -0.6256  |
| O     | -2.8693  | -1.0575  | 0.6943   |
| H     | -3.5380  | -1.5745  | 0.2244   |
| H     | -2.3783  | -1.6687  | 1.2724   |

**Figure 11, transition state 1**
Absolute Energy = -1701.55792713 Hartrees
Cartesian Coordinates

| V     | -1.2429  | -0.3415  | -0.6726  |
| O     | -1.9605  | -1.1591  | -1.8504  |

S22
Figure 11, intermediate
Absolute Energy = -1701.55812653 Hartrees
Cartesian Coordinates
N 1.0052 -1.7109 0.5571
C 1.4613 -1.2724 -0.5628
O -1.5684 1.2590 -0.7595
H 2.4657 -1.5744 -0.8657
O -0.2917 -1.2678 0.7732
N 0.7245 -0.3361 -1.2938
H 1.2465 0.9227 -0.8336
H 0.9123 -0.3801 -2.2934
O 1.7084 1.8642 -0.4406
H 2.2077 1.6745 0.4171
O 2.9935 1.3376 1.7644
H 3.9387 1.5165 1.8172
H 2.8520 0.4498 2.1884
H 0.9849 2.5600 -0.2749
H 2.0195 -1.5336 2.0454
O 2.5941 -1.1346 2.7480
H 2.1175 -1.2542 3.5774
O -0.2994 3.4310 -0.0441
H -0.9486 2.7093 -0.2731
H -0.4854 4.1656 -0.6371
H -2.7089 -0.8670 0.8241
H -3.3882 -1.4145 0.4070
H -2.1565 -1.4569 1.3710

Figure 11, transition state 2
Absolute Energy = -1701.55148707 Hartrees
Cartesian Coordinates
V -1.2262 -0.3433 -0.6988
O -1.9891 -1.1878 -1.8282
N 1.0319 -1.6868 0.5495
C 1.4667 -1.2838 -0.5960
O -1.5470 1.2620 -0.8217
H 2.4650 -1.5990 -0.9070
O -0.2668 -1.2297 0.7610
N 0.7168 -0.3887 -1.3417
H 1.2897 1.0092 -0.7902
H 0.9287 -0.4112 -2.3360
O 1.7059 1.8836 -0.3881
H 2.2018 1.6679 0.4796
O 2.9568 1.3501 1.7873
H 3.9042 1.5224 1.8230
H 2.8162 0.4532 2.2034
H 0.9469 2.5688 -0.2239
H 2.0147 -1.5016 2.0101
O 2.5816 -1.1104 2.7300
H 2.1000 -1.2511 3.5531
O -0.3025 3.3733 -0.0136
H -0.9439 2.6484 -0.2898
H -0.4691 4.1253 -0.5938
O -2.6740 -0.8071 0.8421
H -3.3572 -1.3666 0.4478
H -2.1095 -1.3834 1.3917

Figure 11, intermediate
Absolute Energy = -1701.55812653 Hartrees
Cartesian Coordinates

Figure 11, transition state 2
Absolute Energy = -1701.55148707 Hartrees
Cartesian Coordinates

S23
<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>2.5005</td>
<td>-0.6880</td>
<td>0.3052</td>
</tr>
<tr>
<td>C</td>
<td>2.8637</td>
<td>-0.3965</td>
<td>-0.9103</td>
</tr>
<tr>
<td>O</td>
<td>-0.1179</td>
<td>2.1347</td>
<td>-1.1491</td>
</tr>
<tr>
<td>H</td>
<td>3.8595</td>
<td>-0.7090</td>
<td>-1.2338</td>
</tr>
<tr>
<td>O</td>
<td>1.1972</td>
<td>-0.2445</td>
<td>0.5388</td>
</tr>
<tr>
<td>N</td>
<td>2.0360</td>
<td>0.3290</td>
<td>-1.6991</td>
</tr>
<tr>
<td>H</td>
<td>2.7714</td>
<td>2.0533</td>
<td>-0.9095</td>
</tr>
<tr>
<td>H</td>
<td>2.2821</td>
<td>0.3582</td>
<td>-2.6823</td>
</tr>
<tr>
<td>O</td>
<td>3.1593</td>
<td>2.8113</td>
<td>-0.4175</td>
</tr>
<tr>
<td>H</td>
<td>3.6910</td>
<td>2.4751</td>
<td>0.7332</td>
</tr>
<tr>
<td>O</td>
<td>4.1864</td>
<td>2.2173</td>
<td>1.7078</td>
</tr>
<tr>
<td>H</td>
<td>5.1242</td>
<td>2.4423</td>
<td>1.6656</td>
</tr>
<tr>
<td>H</td>
<td>4.0568</td>
<td>1.1532</td>
<td>2.0413</td>
</tr>
<tr>
<td>H</td>
<td>2.4200</td>
<td>3.4898</td>
<td>-0.3513</td>
</tr>
<tr>
<td>H</td>
<td>3.3327</td>
<td>-0.4987</td>
<td>1.5187</td>
</tr>
<tr>
<td>O</td>
<td>3.9061</td>
<td>-0.1167</td>
<td>2.3389</td>
</tr>
<tr>
<td>H</td>
<td>3.3989</td>
<td>-0.2666</td>
<td>3.1463</td>
</tr>
<tr>
<td>O</td>
<td>1.0344</td>
<td>4.3341</td>
<td>-0.8520</td>
</tr>
<tr>
<td>H</td>
<td>0.8767</td>
<td>5.0657</td>
<td>-0.8725</td>
</tr>
<tr>
<td>O</td>
<td>-1.2034</td>
<td>0.2047</td>
<td>0.7015</td>
</tr>
<tr>
<td>H</td>
<td>-1.8996</td>
<td>-0.3767</td>
<td>0.3656</td>
</tr>
<tr>
<td>H</td>
<td>-0.6172</td>
<td>-0.3393</td>
<td>1.2601</td>
</tr>
</tbody>
</table>

**Figure 11, product**

Absolute Energy = -1701.58206042 Hartrees

Cartesian Coordinates

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>-1.5381</td>
<td>-0.6618</td>
<td>-0.8354</td>
</tr>
<tr>
<td>O</td>
<td>-2.6368</td>
<td>-1.6383</td>
<td>-1.4788</td>
</tr>
<tr>
<td>N</td>
<td>0.9651</td>
<td>-1.4151</td>
<td>0.3392</td>
</tr>
<tr>
<td>C</td>
<td>1.1923</td>
<td>-1.4926</td>
<td>-0.9522</td>
</tr>
<tr>
<td>O</td>
<td>-1.7168</td>
<td>0.8539</td>
<td>-1.3899</td>
</tr>
<tr>
<td>H</td>
<td>2.1991</td>
<td>-1.7540</td>
<td>-1.2805</td>
</tr>
<tr>
<td>O</td>
<td>-0.3145</td>
<td>1.0832</td>
<td>0.6876</td>
</tr>
<tr>
<td>N</td>
<td>0.1719</td>
<td>-1.2552</td>
<td>-1.7567</td>
</tr>
<tr>
<td>H</td>
<td>2.7870</td>
<td>2.9542</td>
<td>-0.3137</td>
</tr>
<tr>
<td>H</td>
<td>0.3430</td>
<td>-1.3509</td>
<td>-2.7491</td>
</tr>
<tr>
<td>O</td>
<td>2.1661</td>
<td>2.8944</td>
<td>-0.4202</td>
</tr>
<tr>
<td>H</td>
<td>2.5892</td>
<td>1.9623</td>
<td>1.7996</td>
</tr>
<tr>
<td>O</td>
<td>2.8792</td>
<td>1.4451</td>
<td>2.5906</td>
</tr>
<tr>
<td>H</td>
<td>3.5159</td>
<td>2.0025</td>
<td>3.0497</td>
</tr>
<tr>
<td>H</td>
<td>2.9849</td>
<td>-0.2613</td>
<td>2.4490</td>
</tr>
<tr>
<td>H</td>
<td>1.2701</td>
<td>2.9327</td>
<td>0.0027</td>
</tr>
<tr>
<td>H</td>
<td>1.6729</td>
<td>-1.4394</td>
<td>1.0958</td>
</tr>
<tr>
<td>O</td>
<td>2.9425</td>
<td>-1.2352</td>
<td>2.2794</td>
</tr>
<tr>
<td>H</td>
<td>2.8544</td>
<td>-1.6495</td>
<td>3.1448</td>
</tr>
<tr>
<td>O</td>
<td>-0.1889</td>
<td>3.0468</td>
<td>-0.8859</td>
</tr>
<tr>
<td>H</td>
<td>-0.7455</td>
<td>2.2519</td>
<td>-1.0725</td>
</tr>
<tr>
<td>H</td>
<td>-0.8099</td>
<td>3.7644</td>
<td>-0.7218</td>
</tr>
<tr>
<td>O</td>
<td>-2.6860</td>
<td>-0.4784</td>
<td>0.9836</td>
</tr>
<tr>
<td>H</td>
<td>-3.4160</td>
<td>-1.1109</td>
<td>0.9330</td>
</tr>
<tr>
<td>H</td>
<td>-2.0769</td>
<td>-0.7892</td>
<td>1.6746</td>
</tr>
</tbody>
</table>

**Complex S1**

Absolute Energy = -1513.230730 Hartrees

Cartesian Coordinates

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>2.298649</td>
<td>9.569206</td>
<td>12.238981</td>
</tr>
<tr>
<td>O</td>
<td>0.404562</td>
<td>8.835654</td>
<td>12.575136</td>
</tr>
</tbody>
</table>
Complex S2
Absolute Energy = -1513.233497 Hartrees
Cartesian Coordinates

Complex S3
Absolute Energy = -1513.218789 Hartrees
Cartesian Coordinates