L-Edge X-Ray Absorption Study of Mononuclear Vanadium Complexes and Spectral Predictions Using a Restricted Open Shell Configuration Interaction Ansatz

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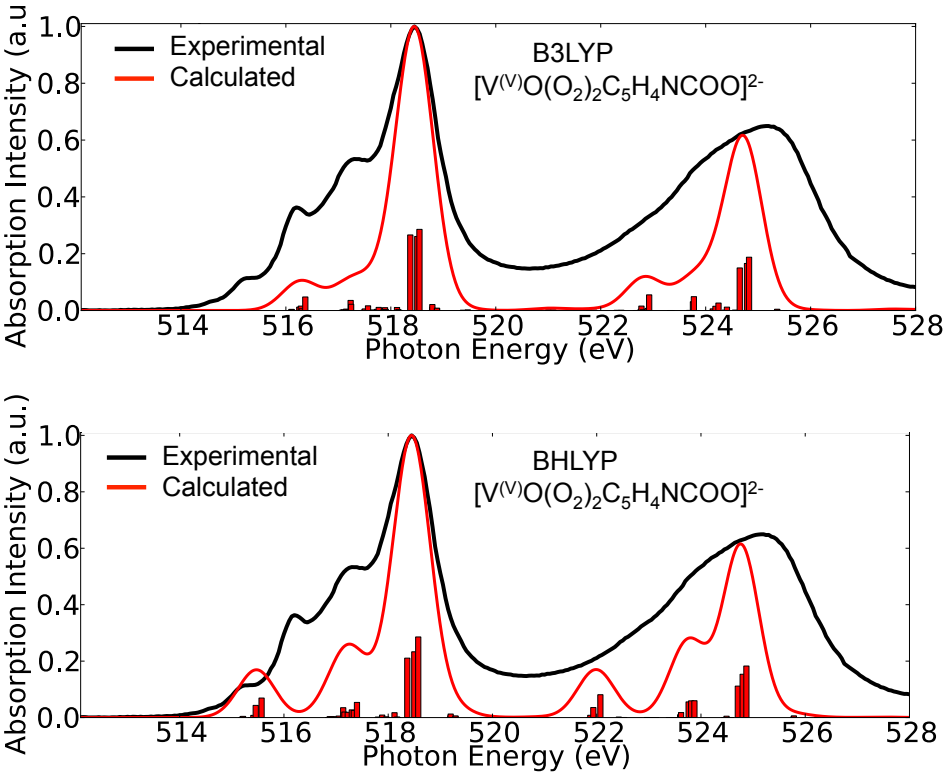

Figure S1
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS(bottom) calculated spectra for complex **1**.

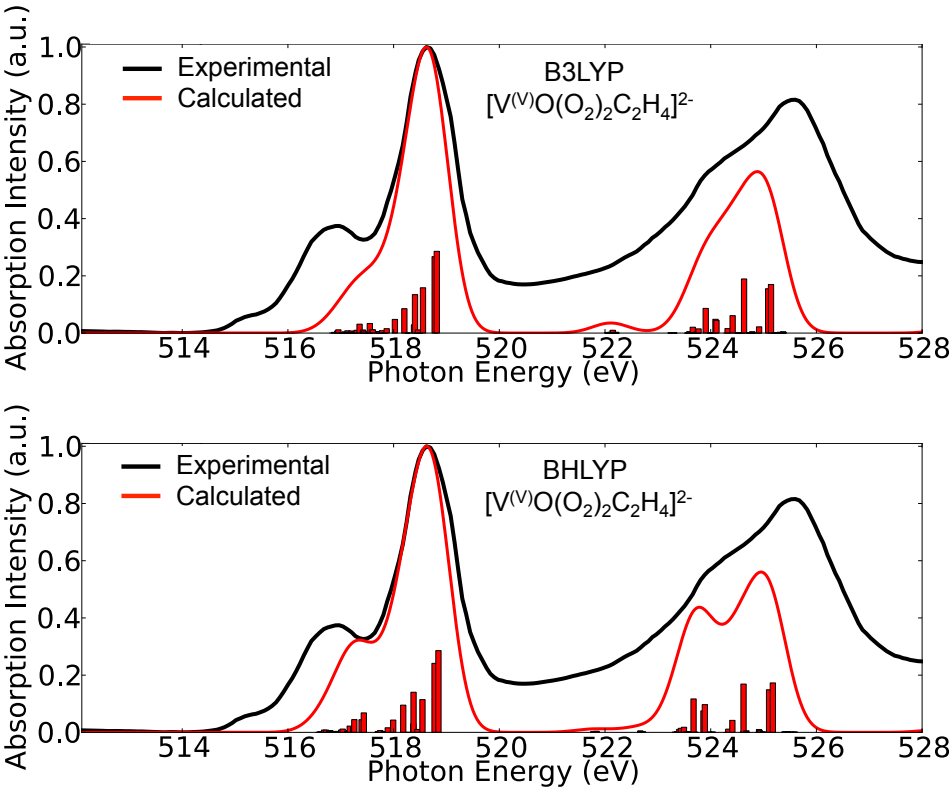

Figure S2
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS(bottom) calculated spectra for complex **2**.

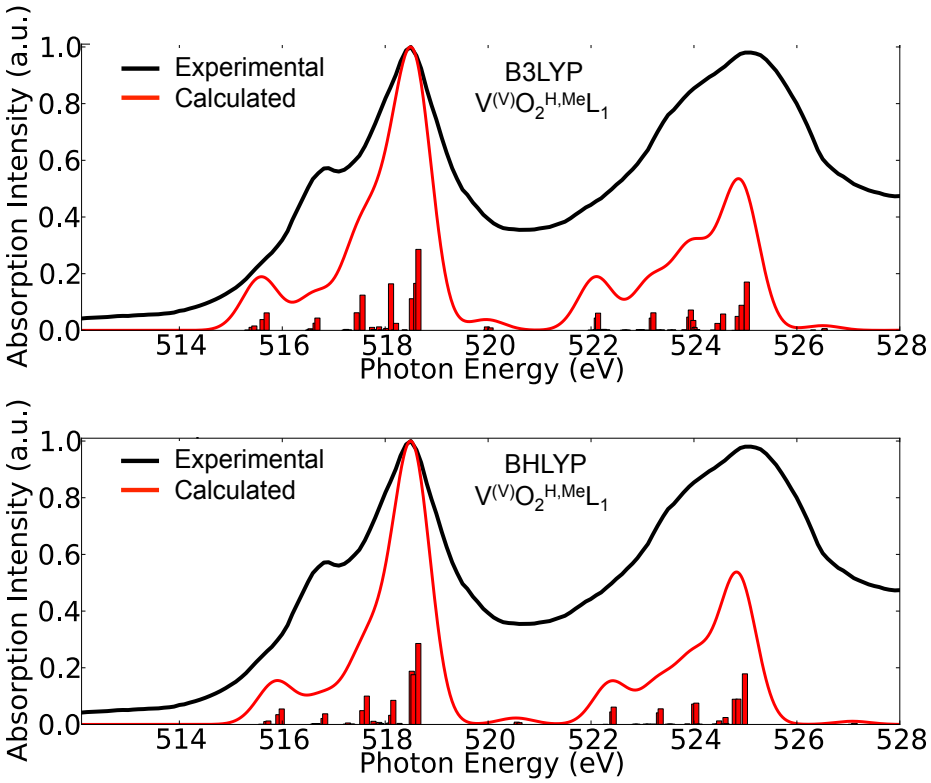

Figure S3
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS (bottom) calculated spectra for complex **3**.

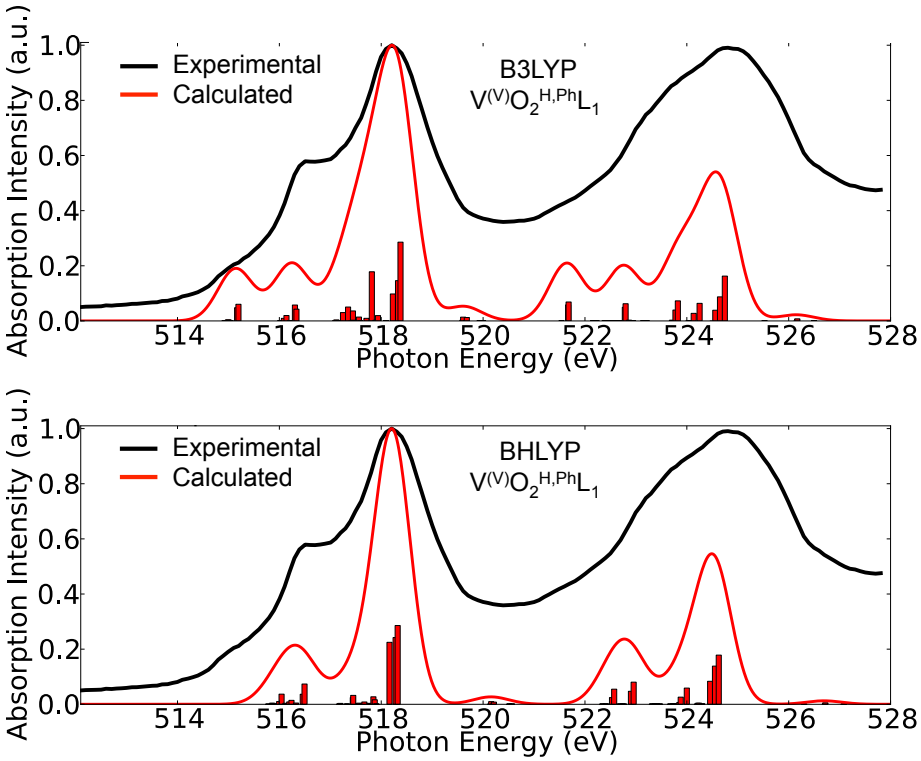

Figure S4

Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS (bottom) calculated spectra for complex **4**.

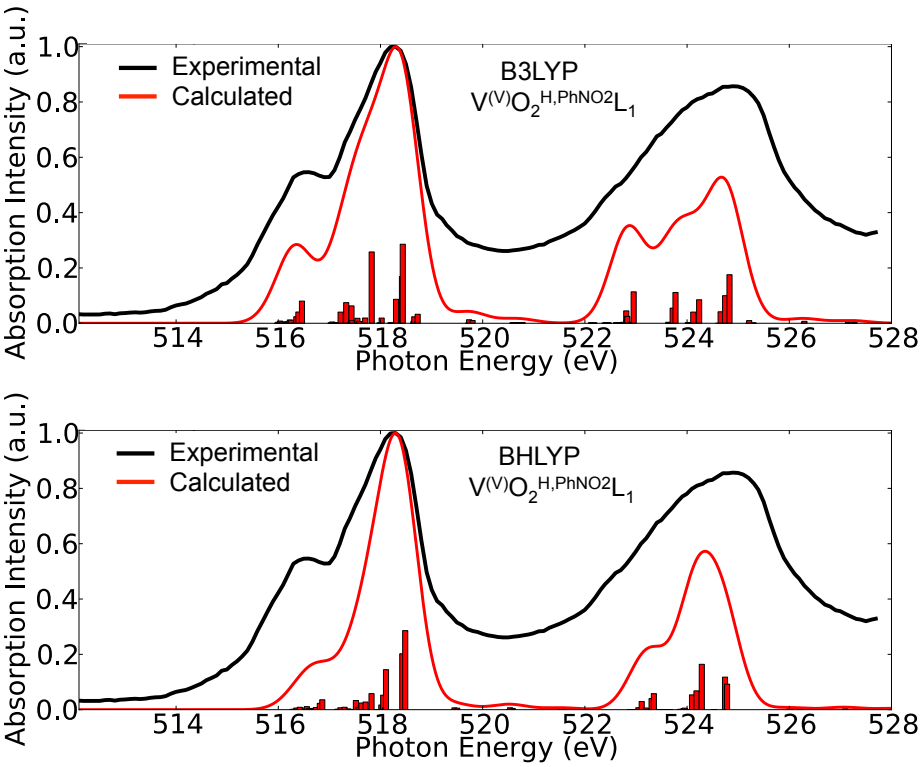

Figure S5
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS (bottom) calculated spectra for complex **5**.

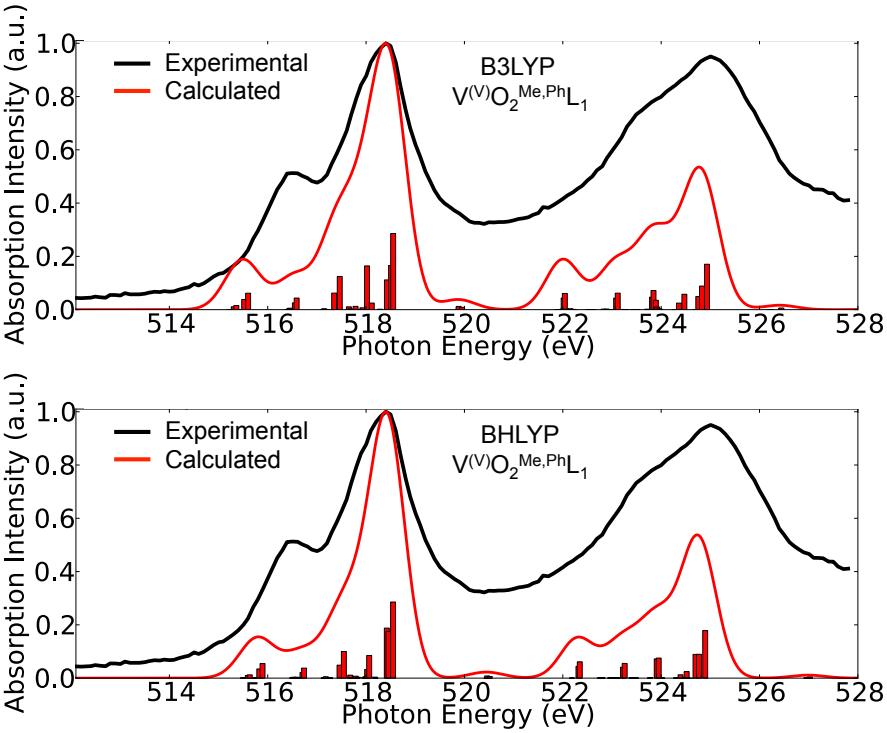

Figure S6
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS (bottom) calculated spectra for complex **6.**

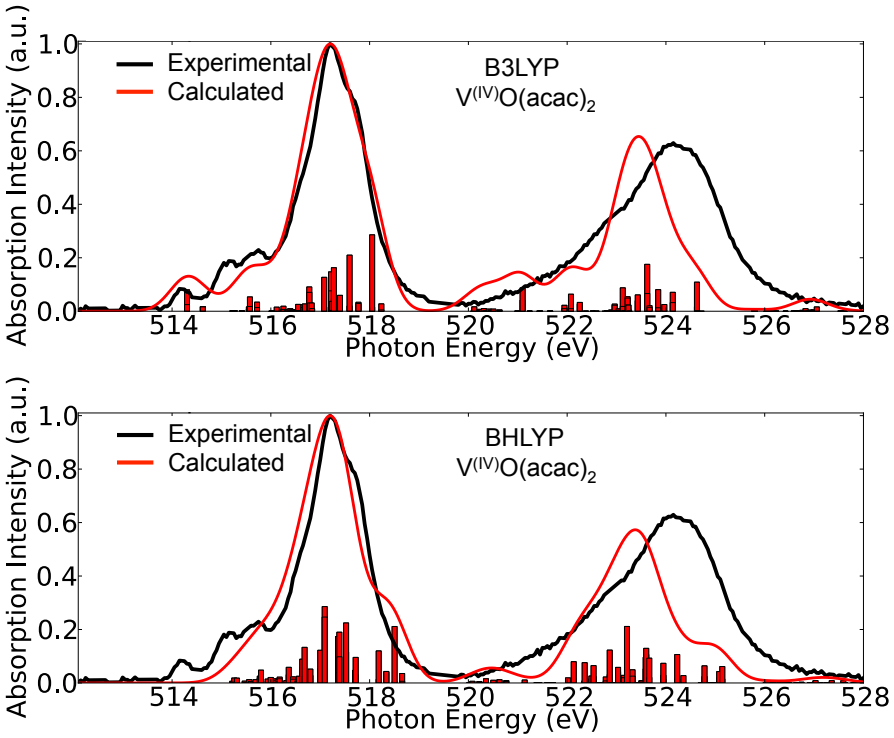

Figure S7
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS (bottom) calculated spectra for complex **7**.

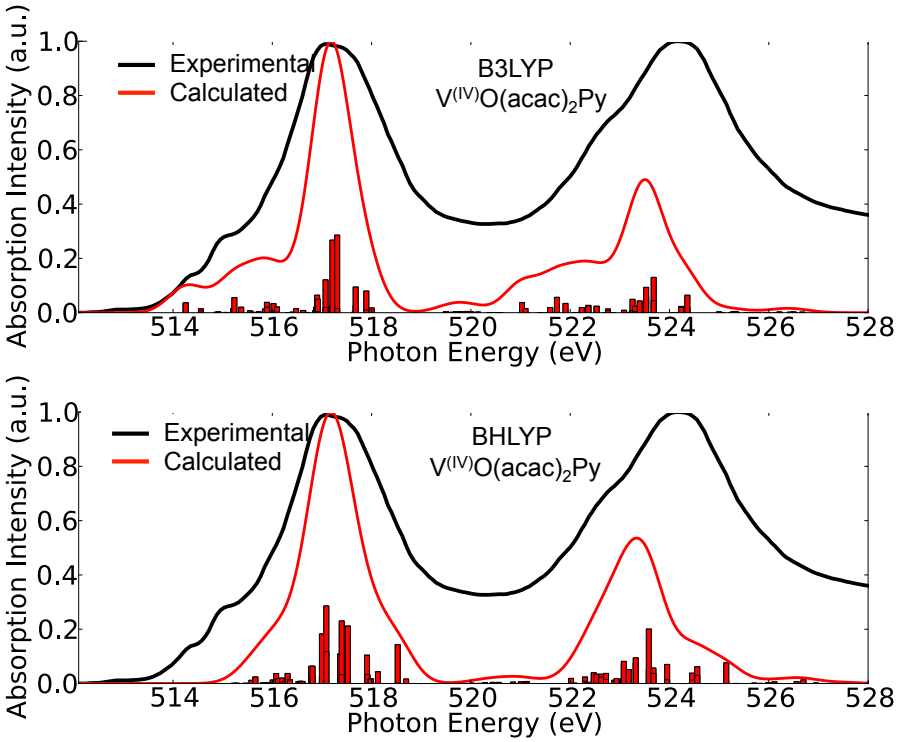

Figure S8
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS (bottom) calculated spectra for complex **8**.

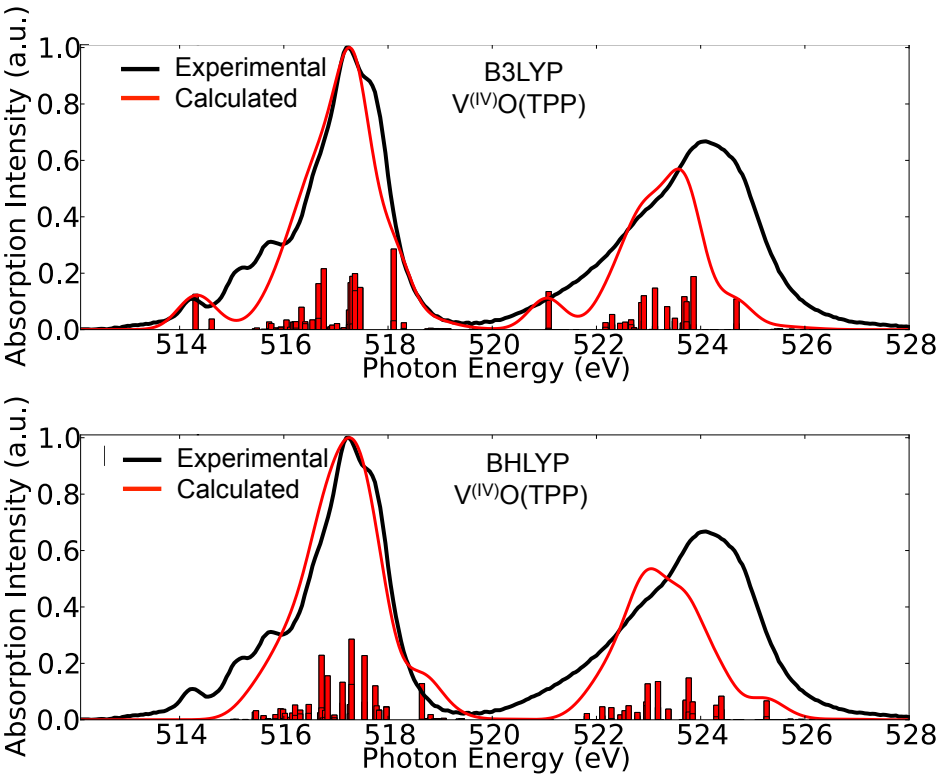

Figure S9
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS (bottom) calculated spectra for complex **9**.

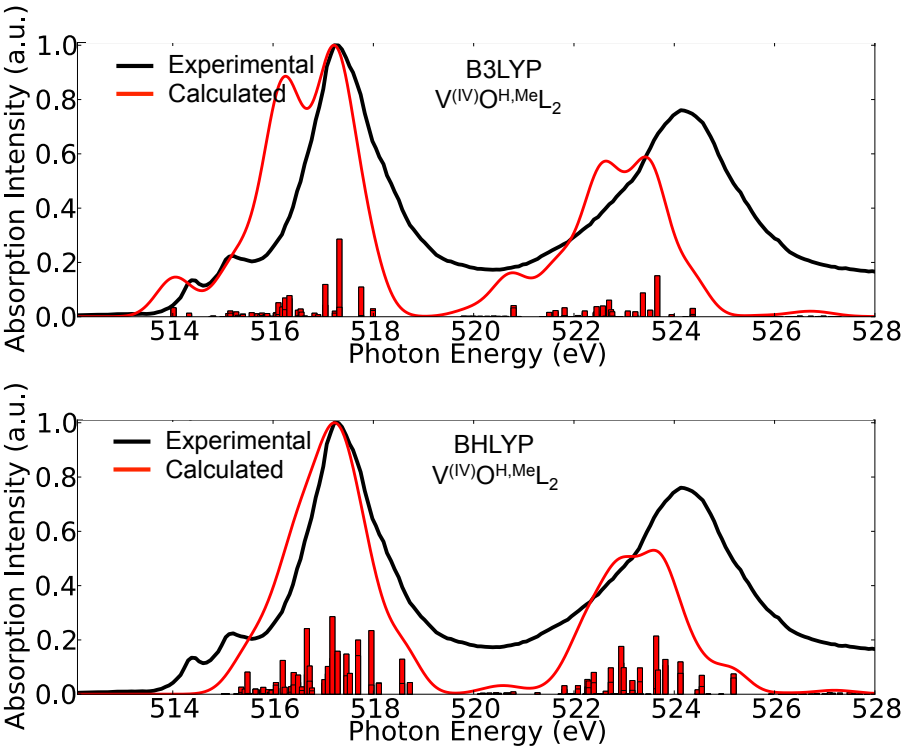

Figure 10
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS (bottom) calculated spectra for complex **10**.

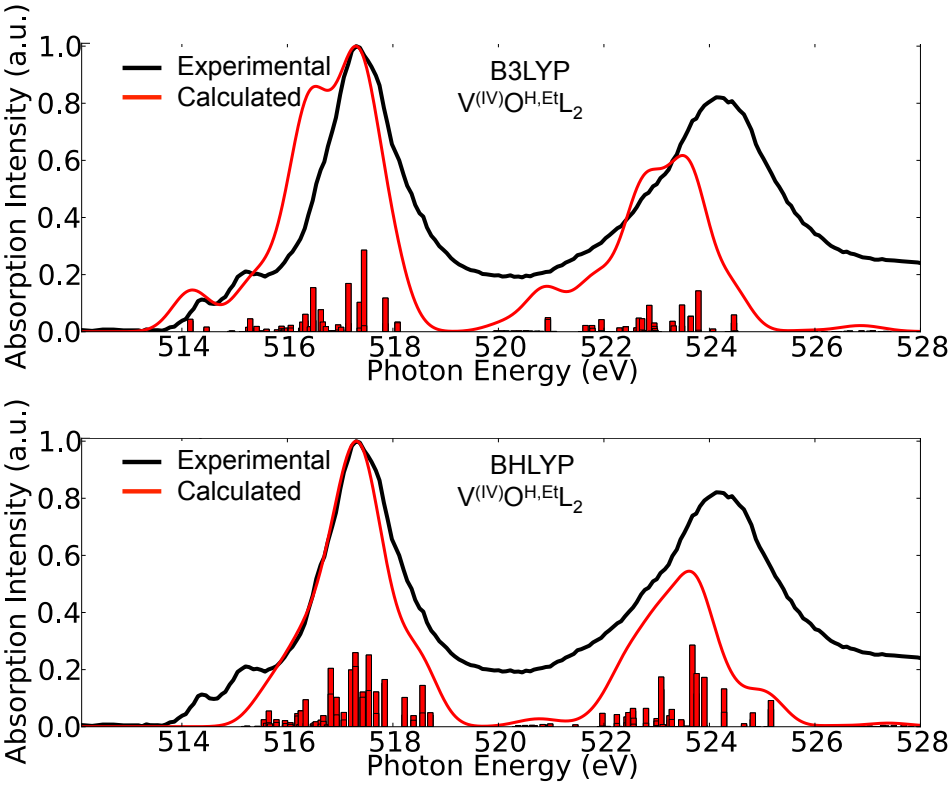

Figure S11
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS (bottom) calculated spectra for complex **11**.

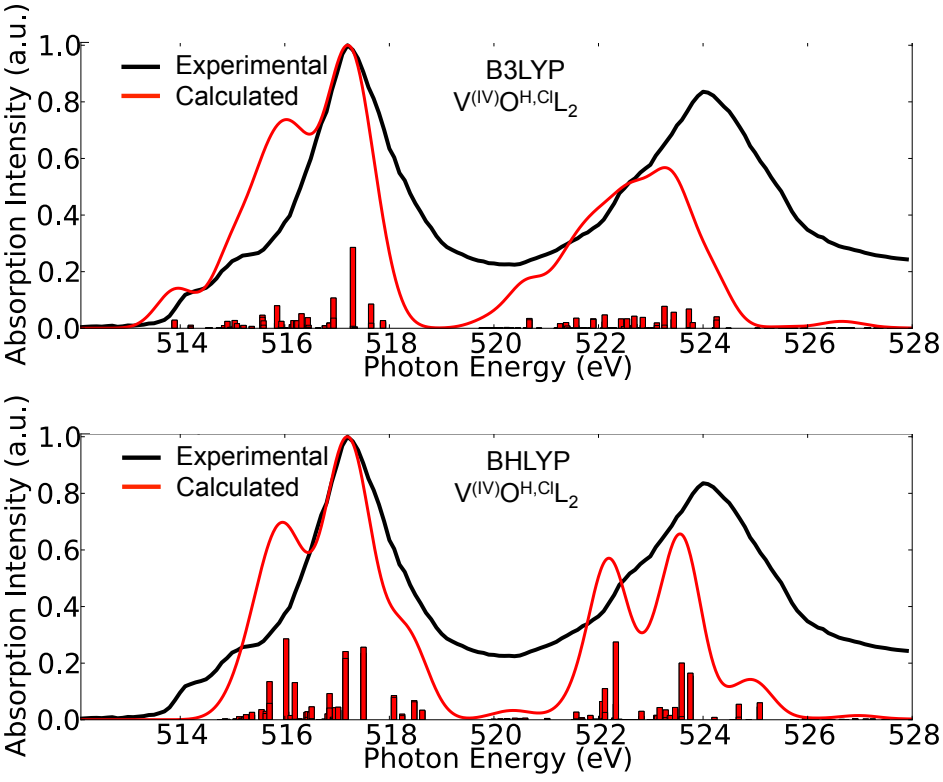

Figure S12
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS (bottom) calculated spectra for complex **12**.

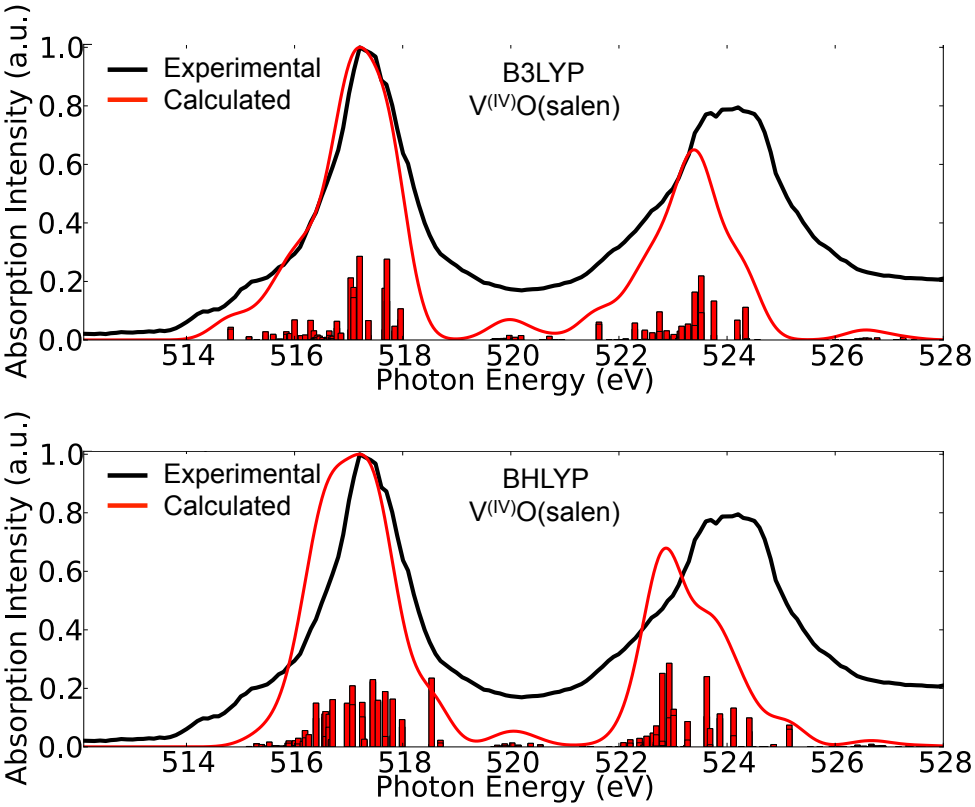

Figure S13
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS (bottom) calculated spectra for complex **13**.

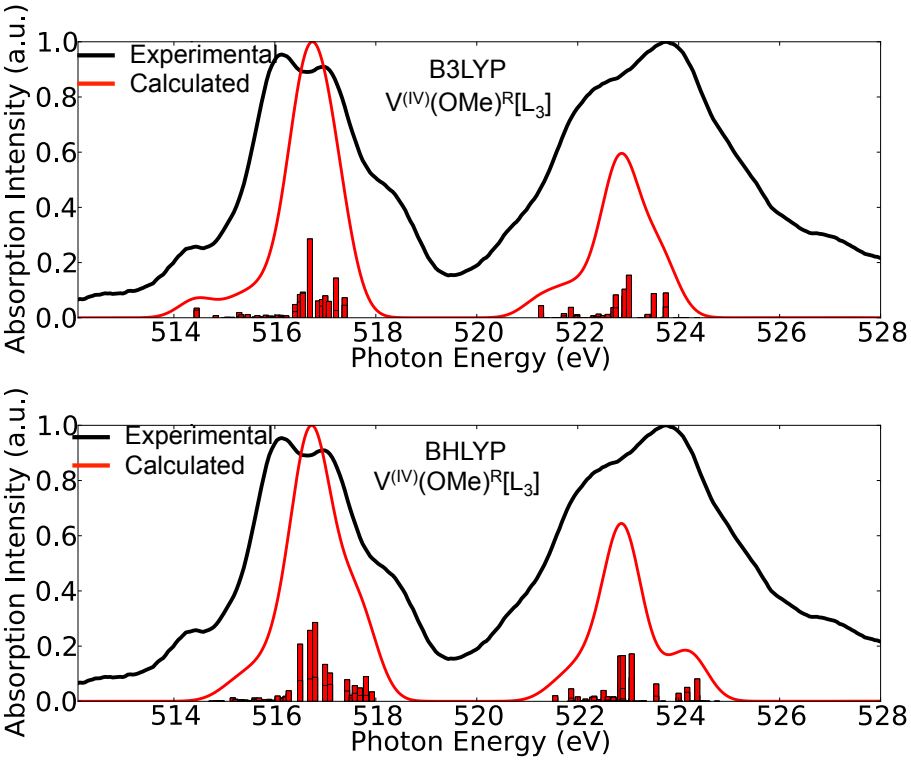

Figure S14
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS (bottom) calculated spectra for complex **14**.

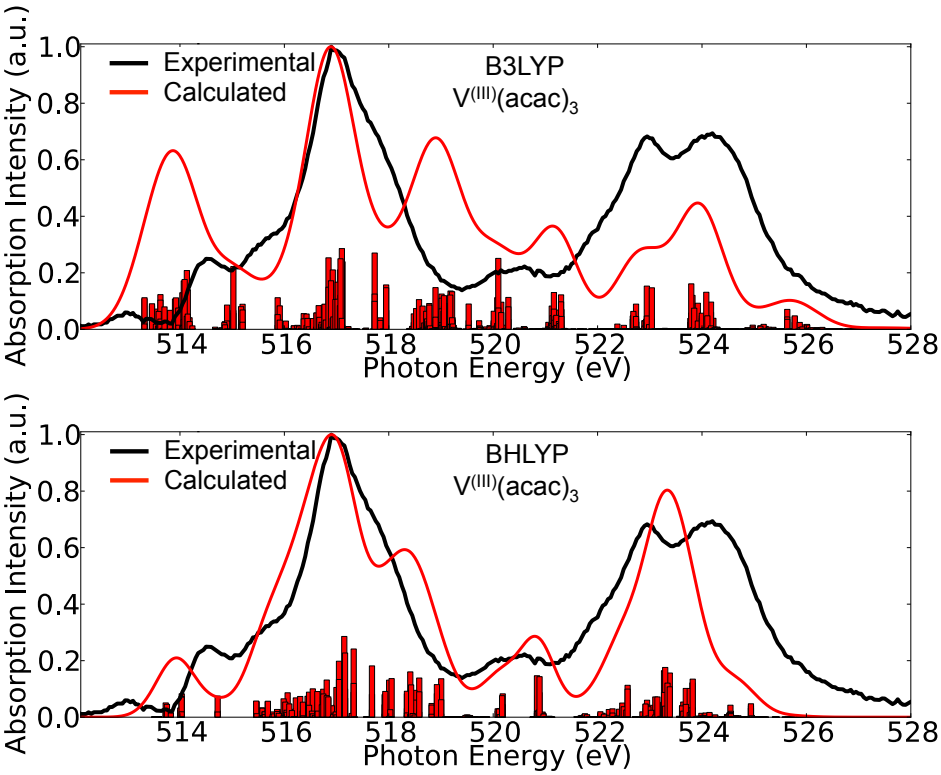

Figure S15
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS (bottom) calculated spectra for complex **15**.

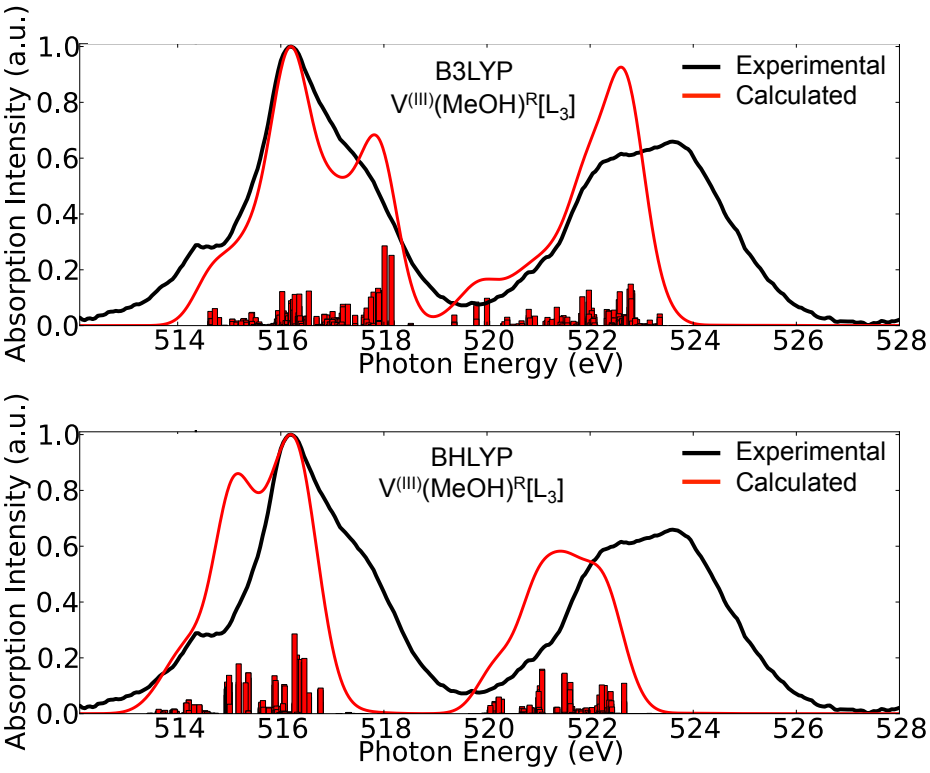

Figure S16
Comparison between B3LYP/ROCIS (top) and BHLYP/ROCIS (bottom) calculated spectra for complex **16**.

Table S1 Selected experimental vs calculated bond lengths**.**

Complex	Distance	Experimental (Å)	Calculated (Å)
1	V-O_{oxo}	1.59	1.60
	V-O_{peroxo}	1.74	1.75
	V-O_{av}	2.29	2.38
	V-N	2.12	2.13
2	V-O_{oxo}	1.63	1.64
	V-O_{peroxo}	1.78	1.75
	V-O_{av}	2.35	2.37
3	V-O_{oxo}	1.62	1.64
	V-O_{av}	1.94	1.97
	V-N_{av}	2.11	2.17
7	V-O_{oxo}	1.58	1.59
	V-O_{av}	1.97	1.99
8	V-O_{oxo}	1.59	1.60
	V-O_{av}	2.22	2.02
	V-N	2.49	2.42
9	V-O_{oxo}	1.59	1.58
	V-N_{av}	2.07	2.08
10	V-O_{oxo}	1.59	1.61
	V-O_{av}	1.95	1.98
	V-N_{av}	2.06	2.09
13	V-O_{oxo}	1.59	1.61
	V-O_{av}	1.95	1.97
	V-N_{av}	2.07	2.10
14	V-$O_{methoxy}$	1.78	1.81
	V-O_{av}	1.81	1.82
	V-N	2.27	2.26
15	V-O_{av}	1.97	1.97
16	V-$O_{methanol}$	2.13	2.16
	V-O_{av}	1.88	1.86
	V-N	2.10	2.11

Effect of oxidation state and ligand strength (Complexes 1-14)

As discussed above the V L-edge spectroscopy is sensitive to changes of the effective nuclear charge on the metal center. In fact, the experimental spectra shift to lower energies as the effective nuclear charge Z_{eff} of the metal oxidation state decreases. This is further observed theoretically and hence, the linear relationship between calculated and experimental energies (figure 4) is divided in regions according to the vanadium formal oxidation state. As can be

seen in figure 5 for the $V^{(V)}$ and $V^{(IV)}$ cases the corresponding spectral regions are well separated. In fact the V L-edge spectra of $V^{(V)}$ complexes appear in higher energies than those of $V^{(IV)}$. The same trend is observed in the cases of $V^{(IV)}$ and $V^{(III)}$ complexes as well, however, these regions are not well distinguished and thus, they partially overlap. Furthermore, in complexes with the same oxidation state the energy position of the L_3 maximum for either the experimentally observed, or the calculated V L-edge spectra is widely distributed. This indicates that the V L-edge spectral regions are also sensitive to the ligand coordination environment and the ligand field strength. To explore this correlation further we have chosen fourteen $V^{(IV)}$ and $V^{(V)}$ complexes bearing a V=O bond. For these complexes a comparison of the calculated Löwdin bond orders as a function of the energy position of the L_3 calculated maximum $\Delta E^{L_3^{max}}$ was made. As is illustrated in figure S17, for this set of complexes a quadratic distribution of the Löwdin bond orders with respect to the corresponding $\Delta E^{L_3^{max}}$ is observed.

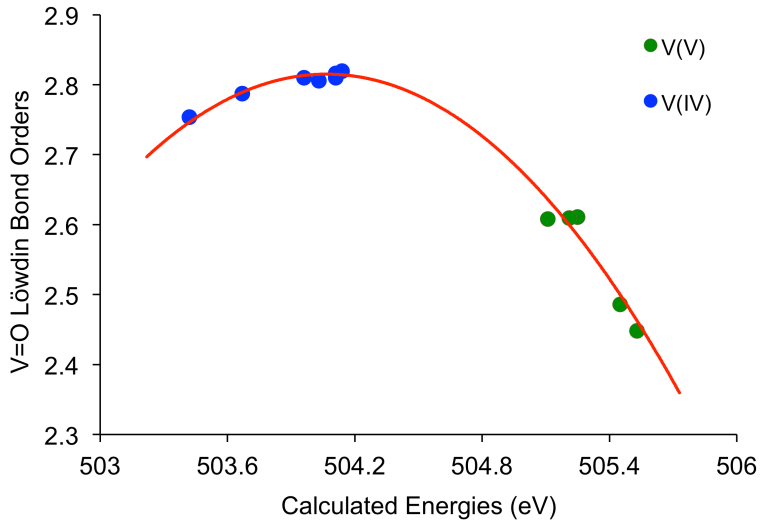

Figure S17

Relation between V=O Löwdin bond orders and the calculated energies at the maximum of the V L_3 spectra ($\Delta E^{L_3^{max}}$) for complexes **1-14**. Blue and green points refer to $V^{(IV)}$ and $V^{(V)}$ complexes respectively. The solid red line represents a second order polynomial fit with: $y = -0.164x^2 + 165.96x - 41825$ and $R^2 = 0.99$.

In fact, as the V=O bond becomes stronger and consequently, as more and more charge is transferred from the O^{2-} ligand to the vanadium center, lower oxidation states with extended π acceptor ligands are preferred and vise versa. Therefore, strong π donor ligands like those in the cases of complexes **1** and **2** will probe the $V^{(V)}$ oxidation state. Likewise, strong π acceptor ligands like those in complexes **7** and **9** will probe the $V^{(IV)}$ oxidation state. In addition, intermediate cases exist as well and the net result is the observed extended distribution of these properties along the calculated $\Delta E_{t_2}^{max}$. It can be concluded that the metal L-edge spectroscopy is indeed a sensitive probe for the metal oxidation state as well as the ligand coordination environment. Much more work is obviously necessary before the potential of such correlation can be fully established in a way similar to, say, the use of the Mössbauer isomer shift, in the case of iron complexes.[1,2]

(1) Römelt, M.; Ye, S.; Neese, F. *Inorganic Chemistry* **2008**, *48*, 784.
(2) Sinnecker, S.; Slep, L. D.; Bill, E.; Neese, F. *Inorganic Chemistry* **2005**, *44*, 2245.

Coordinates of the optimized molecules

1 $[VO(O_2)_2C_5H_4NCOO]^{2-}$

V	9.072000000	8.131000000	0.339000000
O	8.373000000	9.415000000	-0.311000000
O	8.377000000	8.253000000	2.102000000
O	7.661000000	7.295000000	1.259000000
O	8.975000000	6.835000000	-1.041000000
O	10.201000000	7.621000000	-1.123000000
O	10.439000000	6.646000000	1.420000000
O	12.322000000	6.468000000	2.549000000
N	10.734000000	9.236000000	1.063000000
C	11.481000000	7.098000000	1.925000000
C	11.710000000	8.579000000	1.706000000
C	12.850000000	9.244000000	2.198000000
C	12.971000000	10.599000000	1.997000000
C	11.966000000	11.262000000	1.360000000
C	10.833000000	10.554000000	0.887000000
H	13.502000000	8.765000000	2.682000000
H	13.756000000	11.098000000	2.277000000
H	12.008000000	12.206000000	1.244000000
H	10.134000000	11.022000000	0.443000000

2 $[VO(O_2)_2C_2O_4]^{2-}$

V	-4.501042	-1.672590	-5.731111
C	-4.685104	-2.385652	-8.615963
C	-4.152058	-3.746297	-8.019721
O	-6.193129	-2.592713	-5.641906
O	-5.385837	-2.731099	-4.426610
O	-2.865948	-1.894870	-4.791843
O	-2.638724	-1.409457	-6.155896
O	-4.876018	-1.431346	-7.765201
O	-3.962067	-3.745677	-6.764551
O	-4.897142	-2.276894	-9.842136
O	-3.959839	-4.705397	-8.813760
O	-4.960091	-0.132009	-5.361304

3 $[V(O)_2{}^{H,Me}L_3)]$

V	4.021248000	0.910706000	2.330452000
O	3.795778000	2.028440000	3.903052000
O	4.418277000	-1.966522000	3.490090000
O	5.305286000	1.566355000	1.590116000
O	2.671205000	1.200676000	1.480917000
N	4.209208000	-0.588053000	3.895138000
N	4.308029000	-0.976907000	1.456254000
C	3.805322000	1.948592000	5.201534000
C	3.617782000	3.124540000	5.974554000
C	3.620567000	3.066155000	7.355637000
C	3.807488000	1.846630000	8.045614000
C	3.990869000	0.688869000	7.319868000
C	3.994838000	0.707444000	5.901195000
C	4.185377000	-0.510514000	5.199695000
C	4.453567000	-2.048779000	2.144058000
H	4.339452000	-1.080527000	0.443183000
H	3.473417000	4.065533000	5.443463000
H	3.475003000	3.985249000	7.927016000
H	3.806065000	1.825280000	9.135318000
H	4.137107000	-0.267342000	7.828382000
H	4.319539000	-1.432732000	5.777993000
C	4.666982000	-3.444441000	1.654493000
H	5.622559000	-3.834389000	2.035945000
H	3.861987000	-4.099220000	2.020186000
H	4.679226000	-3.458820000	0.557750000

4 $[V(O)_2{}^{H,Ph}L_3)]$

V	3.553801000	0.862606000	2.339100000
O	3.502896000	1.974531000	3.933344000
O	4.482117000	-1.930877000	3.394726000
O	4.567271000	1.667865000	1.363246000
O	2.036429000	0.967378000	1.778336000
N	4.199248000	-0.582425000	3.834172000
N	3.917984000	-0.979758000	1.418314000
C	3.732518000	1.907283000	5.211757000
C	3.545417000	3.062635000	6.015810000
C	3.780733000	3.018143000	7.377108000
C	4.211809000	1.833047000	8.016097000
C	4.401083000	0.696069000	7.259760000
C	4.170784000	0.701398000	5.859714000
C	4.377691000	-0.494591000	5.126549000
C	4.308090000	-2.026996000	2.056595000
H	3.834804000	-1.070762000	0.407082000
H	3.212294000	3.976474000	5.523562000
H	3.629349000	3.920695000	7.972855000
H	4.390742000	1.821747000	9.091129000
H	4.733346000	-0.233123000	7.729445000
C	4.600096000	-3.359700000	1.509205000
C	5.424353000	-4.261285000	2.201885000
C	4.057143000	-3.734189000	0.269907000
C	5.707821000	-5.510589000	1.654686000
C	4.343637000	-4.983018000	-0.273833000
C	5.171490000	-5.873005000	0.416539000
H	5.844233000	-3.974874000	3.165512000
H	3.397138000	-3.050546000	-0.266822000
H	6.353183000	-6.204612000	2.194576000
H	3.914896000	-5.266739000	-1.235619000
H	5.395155000	-6.851949000	-0.009968000
H	4.704245000	-1.390499000	5.668372000

5 $[V(O)_2{}^{H,PhNO2}L_3)]$

V	3.603357000	0.891231000	2.331405000
O	3.618694000	2.002302000	3.923015000
O	4.466854000	-1.931125000	3.367972000
O	4.601805000	1.676610000	1.324843000
O	2.074825000	1.006850000	1.805918000
N	4.204476000	-0.580753000	3.818145000
N	3.935502000	-0.953063000	1.393984000
C	3.788272000	1.910068000	5.209551000
C	3.616490000	3.062653000	6.020152000
C	3.796331000	2.992140000	7.388583000
C	4.156300000	1.783168000	8.027852000
C	4.331466000	0.648860000	7.265305000
C	4.154776000	0.679558000	5.857120000
C	4.346574000	-0.513551000	5.117313000
C	4.298572000	-2.010167000	2.030337000
H	3.858091000	-1.032052000	0.381147000
H	3.338584000	3.994683000	5.527913000
H	3.656505000	3.892378000	7.990424000
H	4.292437000	1.752938000	9.108841000
H	4.609812000	-0.297478000	7.735516000
C	4.572312000	-3.345102000	1.473568000
C	5.387534000	-4.257810000	2.162465000
C	4.021792000	-3.702957000	0.232511000
C	5.660175000	-5.505787000	1.613470000
C	4.289798000	-4.947618000	-0.323302000
C	5.108722000	-5.829407000	0.377280000
H	5.811454000	-3.982036000	3.126845000
H	3.368581000	-3.009609000	-0.298668000
H	6.293090000	-6.229087000	2.124885000
H	3.871683000	-5.247057000	-1.282834000
H	4.628751000	-1.424972000	5.658001000
N	5.400517000	-7.170630000	-0.216224000
O	6.116549000	-7.937653000	0.436278000
O	4.906829000	-7.423506000	-1.320205000

6 $[V(O)_2^{Me,Ph}L_3)]$

V	4.021248000	0.910706000	2.330452000
O	3.795778000	2.028440000	3.903052000
O	4.418277000	-1.966522000	3.490090000
O	5.305286000	1.566355000	1.590116000
O	2.671205000	1.200676000	1.480917000
N	4.209208000	-0.588053000	3.895138000
N	4.308029000	-0.976907000	1.456254000
C	3.805322000	1.948592000	5.201534000
C	3.617782000	3.124540000	5.974554000
C	3.620567000	3.066155000	7.355637000
C	3.807488000	1.846630000	8.045614000
C	3.990869000	0.688869000	7.319868000
C	3.994838000	0.707444000	5.901195000
C	4.185377000	-0.510514000	5.199695000
C	4.453567000	-2.048779000	2.144058000
H	4.339452000	-1.080527000	0.443183000
H	3.473417000	4.065533000	5.443463000
H	3.475003000	3.985249000	7.927016000
H	3.806065000	1.825280000	9.135318000
H	4.137107000	-0.267342000	7.828382000
H	4.319539000	-1.432732000	5.777993000
C	4.666982000	-3.444441000	1.654493000
H	5.622559000	-3.834389000	2.035945000
H	3.861987000	-4.099220000	2.020186000
H	4.679226000	-3.458820000	0.557750000

7 $[V(O)(acac)_2]$

V	2.036934000	1.818157000	2.399699000
O	1.227325000	0.046997000	1.947553000
O	3.813022000	0.901639000	2.360998000
O	2.906671000	2.959708000	3.790985000
O	0.320561000	2.106088000	3.381454000
O	1.954385000	2.699962000	1.079562000
C	0.869937000	-2.075176000	0.970389000
C	1.801038000	-0.983859000	1.433157000
C	3.190423000	-1.143562000	1.308730000
C	4.121505000	-0.217152000	1.804818000
C	5.597538000	-0.513840000	1.729540000
C	3.304296000	4.693703000	5.346021000
C	2.352767000	3.795819000	4.597454000
C	0.969744000	3.892164000	4.819024000
C	0.031725000	3.028676000	4.230898000
C	-1.426421000	3.131050000	4.598406000
H	0.254499000	-2.410612000	1.819791000
H	0.182558000	-1.664469000	0.214273000
H	1.414910000	-2.930210000	0.549349000
H	3.565758000	-2.062402000	0.860502000
H	6.098038000	0.293038000	1.172021000
H	6.019537000	-0.515392000	2.746752000
H	5.799166000	-1.478186000	1.244941000
H	4.020956000	4.074233000	5.907405000
H	3.886058000	5.283295000	4.620220000
H	2.779064000	5.368713000	6.034091000
H	0.611969000	4.634457000	5.531065000
H	-2.008948000	3.357435000	3.691275000
H	-1.775788000	2.156457000	4.972917000
H	-1.607229000	3.906268000	5.354710000

8 $[V(O)(acac)_2(Py)]$

C	3.595268000	9.578255000	12.318138000
C	2.686173000	9.749279000	13.377083000
H	3.092673000	10.019674000	14.350888000
C	1.293884000	9.578789000	13.278602000
C	5.071841000	9.775557000	12.568623000
H	5.604253000	8.842550000	12.325928000
H	5.282118000	10.059353000	13.608326000
H	5.455345000	10.552767000	11.888899000
C	0.433704000	9.777921000	14.504298000
H	-0.316156000	10.558246000	14.299257000
H	1.025611000	10.058966000	15.385431000
H	-0.116960000	8.846879000	14.710997000
C	2.505487000	11.978040000	9.943077000
H	3.335289000	11.358124000	9.596416000
C	2.548853000	13.373427000	9.924970000
H	3.436287000	13.888059000	9.554344000
C	1.438703000	14.084305000	10.388631000
H	1.438696000	15.175882000	10.388623000
N	1.438730000	11.294837000	10.388666000
O	1.438759000	7.267991000	10.388676000
O	0.658144000	9.259898000	12.212095000
O	3.283801000	9.260128000	11.116066000
V	1.438742000	8.865685000	10.388663000
C	-0.717793000	9.578264000	8.459185000
C	0.191299000	9.749306000	7.400243000
H	-0.215202000	10.019713000	6.426442000
C	1.583591000	9.578819000	7.498721000
C	-2.194367000	9.775574000	8.208702000
H	-2.726796000	8.842597000	8.451469000
H	-2.404652000	10.059299000	7.168985000
H	-2.577848000	10.552851000	8.888368000
C	2.443771000	9.777991000	6.273033000
H	3.193528000	10.558420000	6.478048000
H	1.851849000	10.058920000	5.391874000
H	2.994564000	8.847011000	6.066398000
C	0.371958000	11.978032000	10.834232000
H	-0.457835000	11.358104000	11.180904000
C	0.328564000	13.373418000	10.852306000
H	-0.558881000	13.888039000	11.222920000
O	2.219333000	9.259912000	8.565222000
O	-0.406325000	9.260119000	9.661251000

9 [V)(O)(TPP)]

V	6.343703000	8.314794000	2.521731000
O	6.052341000	8.215520000	4.082462000
N	8.121127000	7.275436000	2.256909000
N	5.415017000	6.638665000	1.718076000
N	4.750015000	9.417730000	1.776101000
N	7.456693000	10.053379000	2.315173000
C	8.271134000	5.904577000	2.164928000
C	7.240026000	4.994201000	1.929799000
C	5.906766000	5.346750000	1.719654000
C	4.841607000	4.412665000	1.472743000
C	3.701114000	5.140379000	1.311788000
C	4.061159000	6.520643000	1.466483000
C	3.162656000	7.576541000	1.376012000
C	3.486767000	8.920120000	1.517484000
C	2.539654000	9.992991000	1.414982000
C	3.228978000	11.151018000	1.615219000
C	4.603983000	10.791117000	1.833935000
C	5.635805000	11.699958000	2.069505000
C	6.969624000	11.346268000	2.277201000
C	8.045790000	12.284478000	2.450392000
C	9.189062000	11.558367000	2.598535000
C	8.818880000	10.174627000	2.513597000
C	9.719213000	9.119636000	2.594776000
C	9.392372000	7.775502000	2.465671000
C	10.348656000	6.706345000	2.504057000
C	9.656369000	5.548277000	2.314895000
H	10.038929000	4.534596000	2.256316000
H	4.965094000	3.335294000	1.438901000
H	2.694175000	4.791592000	1.107749000
H	1.480658000	9.856016000	1.215622000
H	2.850929000	12.168424000	1.626016000
H	7.928284000	13.362986000	2.433111000
H	10.205859000	11.910185000	2.740601000
H	11.415930000	6.846720000	2.645843000
C	5.296441000	13.145033000	2.095897000
C	4.780907000	13.784124000	0.959596000
C	5.490081000	13.899027000	3.262030000
C	4.466782000	15.142909000	0.986887000
C	5.174082000	15.257230000	3.293093000
C	4.661438000	15.884190000	2.154835000
H	4.637227000	13.204372000	0.046431000
H	5.885634000	13.404458000	4.150538000
H	4.071897000	15.628061000	0.092564000
H	5.324459000	15.829472000	4.210152000
H	4.414739000	16.947097000	2.177797000
C	11.149796000	9.456543000	2.833168000
C	11.640003000	9.560291000	4.139005000
C	12.018312000	9.671691000	1.758078000
C	12.980546000	9.875018000	4.367826000
C	13.359276000	9.986476000	1.984660000
C	13.843677000	10.088825000	3.290708000
H	10.960823000	9.391587000	4.976520000
H	11.635625000	9.590618000	0.739093000
H	13.355049000	9.954013000	5.389804000
H	14.030705000	10.152789000	1.140550000
H	14.892062000	10.334825000	3.468666000
C	1.737085000	7.240707000	1.107621000
C	1.262965000	7.152407000	-0.205173000
C	0.856369000	7.008959000	2.169371000
C	-0.073756000	6.836572000	-0.454501000
C	-0.480696000	6.693434000	1.922284000
C	-0.949069000	6.606348000	0.609258000
H	1.950596000	7.333122000	-1.033359000
H	1.227886000	7.078176000	3.193250000
H	-0.436045000	6.769503000	-1.481761000
H	-1.161381000	6.514097000	2.756204000
H	-1.994406000	6.359427000	0.415356000
C	7.591388000	3.552142000	1.895260000
C	8.114941000	2.920781000	3.032403000
C	7.411524000	2.795574000	0.728772000
C	8.447930000	1.566535000	3.005788000
C	7.747207000	1.442016000	0.698125000
C	8.265702000	0.822324000	1.837699000
H	8.250958000	3.504142000	3.944374000
H	7.013481000	3.284089000	-0.162045000
H	8.848678000	1.087565000	3.900808000
H	7.607265000	0.867429000	-0.219151000
H	8.527231000	-0.237051000	1.815405000

10 [V(O)($H^{Me}L_2$)(O)]

V	9.381698000	3.293238000	7.896238000
N	8.730275000	5.178255000	8.476233000
N	11.003776000	2.088799000	7.416387000
O	10.134086000	3.190732000	9.682950000
O	8.463616000	6.073691000	7.434616000
H	8.872481000	5.576910000	6.663465000
H	10.469489000	2.054571000	11.943633000
O	9.774138000	4.200076000	6.226362000
O	11.616762000	1.438767000	8.492792000
H	11.185981000	1.921640000	9.261014000
H	9.104052000	5.102244000	3.934059000
O	8.084873000	2.380095000	7.759797000
C	8.518144000	5.655571000	9.676953000
C	8.763850000	4.815525000	10.848565000
C	9.576645000	3.642634000	10.812316000
C	9.830995000	2.937087000	12.002355000
C	9.282944000	3.344823000	13.210007000
H	9.489627000	2.775170000	14.117799000
C	8.457591000	4.475409000	13.258660000
H	8.005936000	4.791926000	14.199053000
C	8.213957000	5.189580000	12.094933000
H	7.568269000	6.065287000	12.149237000
C	11.529348000	1.832150000	6.245249000
C	10.972659000	2.455996000	5.045330000
C	10.147086000	3.619604000	5.079810000
C	9.720438000	4.204257000	3.873716000
C	10.065024000	3.653455000	2.647815000
H	9.713864000	4.121664000	1.726543000
C	10.849410000	2.494084000	2.595973000
H	11.108446000	2.042698000	1.638064000
C	11.291387000	1.919127000	3.778256000
H	11.899588000	1.016956000	3.722187000
C	12.703853000	0.895839000	6.165462000
H	13.364458000	1.065240000	7.026546000
H	12.360660000	-0.149997000	6.228617000
H	13.266444000	1.035765000	5.236711000
C	8.029153000	7.071313000	9.813951000
H	8.553765000	7.706684000	9.086746000
H	6.956460000	7.129433000	9.567163000
H	8.192352000	7.460433000	10.823843000

11 $[V(O)(H^{Et}L_2)(O)]$

V	9.361087000	3.265896000	7.952485000
N	8.698653000	5.143896000	8.539323000
N	10.985537000	2.074407000	7.454165000
O	10.130088000	3.161652000	9.731968000
O	8.389400000	6.024552000	7.494823000
H	8.802506000	5.534643000	6.721658000
H	10.523138000	2.048823000	11.996960000
O	9.722347000	4.174916000	6.275860000
O	11.600474000	1.413777000	8.525408000
H	11.177548000	1.897055000	9.297763000
H	9.052385000	5.091252000	3.988231000
O	8.069753000	2.343054000	7.827588000
C	8.502321000	5.620926000	9.742623000
C	8.782052000	4.791262000	10.912317000
C	9.598031000	3.621987000	10.869663000
C	9.883887000	2.930420000	12.060738000
C	9.365588000	3.351940000	13.276575000
H	9.596122000	2.793614000	14.185687000
C	8.540511000	4.482516000	13.333017000
H	8.114159000	4.810139000	14.281356000
C	8.265801000	5.181932000	12.167874000
H	7.618917000	6.056591000	12.225412000
C	11.502579000	1.823825000	6.277807000
C	10.940793000	2.453283000	5.085268000
C	10.105009000	3.608782000	5.125984000
C	9.678097000	4.200120000	3.923236000
C	10.034635000	3.663605000	2.694540000
H	9.683576000	4.136265000	1.775473000
C	10.832061000	2.513372000	2.636322000
H	11.101545000	2.074363000	1.675559000
C	11.274259000	1.932816000	3.815216000
H	11.889916000	1.035894000	3.755633000
C	12.654499000	0.857439000	6.169934000
H	13.254605000	1.097963000	5.283099000
H	13.293325000	0.983285000	7.054818000
C	12.147409000	-0.596885000	6.108930000
H	11.506781000	-0.751571000	5.227702000
H	11.562530000	-0.830586000	7.009345000
H	12.996837000	-1.293517000	6.051559000
C	7.955833000	7.016992000	9.902702000
H	8.288454000	7.432515000	10.862547000
H	8.369475000	7.643572000	9.100830000
C	6.417315000	7.020393000	9.809198000
H	5.974039000	6.403464000	10.605314000
H	6.097370000	6.616757000	8.838510000
H	6.033275000	8.046695000	9.906071000

12 [V(O)($H^{Cl}L_2$)(O)]

V	9.385966000	3.302510000	7.892154000
N	8.747759000	5.208942000	8.452104000
N	10.997408000	2.061200000	7.432022000
O	10.122215000	3.196672000	9.679441000
O	8.517273000	6.101514000	7.418184000
H	8.921137000	5.593359000	6.650670000
H	10.510753000	2.098963000	11.947706000
O	9.799283000	4.193059000	6.224221000
O	11.602023000	1.424325000	8.503348000
H	11.170561000	1.913605000	9.268305000
H	9.226451000	5.169132000	3.939758000
O	8.079555000	2.408039000	7.753857000
C	8.506342000	5.629895000	9.661955000
C	8.768432000	4.835241000	10.854482000
C	9.588565000	3.665390000	10.813081000
C	9.872191000	2.981125000	12.008315000
C	9.354595000	3.410360000	13.221167000
H	9.586116000	2.856420000	14.132562000
C	8.531049000	4.542773000	13.272759000
H	8.110029000	4.879809000	14.220133000
C	8.252595000	5.236709000	12.106889000
H	7.620212000	6.121690000	12.152758000
C	11.461339000	1.792122000	6.243975000
C	10.979258000	2.438550000	5.030455000
C	10.189852000	3.629342000	5.075924000
C	9.818304000	4.255493000	3.873077000
C	10.187721000	3.727030000	2.645355000
H	9.880073000	4.230327000	1.727129000
C	10.942205000	2.547858000	2.585914000
H	11.225750000	2.118866000	1.624737000
C	11.328539000	1.925555000	3.761497000
H	11.922911000	1.014839000	3.711135000
Cl	12.760890000	0.614423000	6.120263000
Cl	7.866865000	7.257064000	9.849544000

13 [V(O)(salen)]

V	3.605889000	5.165503000	1.779513000
O	2.180832000	4.929511000	3.082923000
O	3.014078000	3.566472000	0.820540000
O	2.574266000	0.983772000	0.334007000
O	0.551217000	3.819475000	4.866314000
O	5.037842000	4.825171000	2.401662000
N	3.928453000	5.997744000	-0.091219000
N	3.430075000	7.195024000	2.160604000
C	1.658096000	5.724189000	3.978070000
C	0.764953000	5.168437000	4.949441000
C	0.168701000	5.977795000	5.905314000
H	-0.504827000	5.518606000	6.635610000
C	0.412715000	7.365248000	5.953939000
H	-0.070882000	7.972121000	6.719409000
C	1.262757000	7.932457000	5.029546000
H	1.465456000	9.005625000	5.044417000
C	1.893277000	7.134716000	4.038828000
C	2.750898000	7.785153000	3.101696000
H	2.831705000	8.880970000	3.192734000
C	4.272333000	7.980002000	1.255027000
H	5.325428000	7.778192000	1.511875000
H	4.074711000	9.062948000	1.338961000
C	3.983644000	7.467993000	-0.155450000
H	2.998657000	7.844792000	-0.482330000
H	4.746697000	7.809437000	-0.876508000
C	4.162238000	5.322151000	-1.186904000
H	4.501577000	5.881115000	-2.074960000
C	3.985165000	3.920265000	-1.364158000
C	4.354570000	3.352577000	-2.613779000
H	4.806051000	3.999584000	-3.369185000
C	4.139984000	2.016425000	-2.869618000
H	4.424268000	1.575003000	-3.824935000
C	3.538623000	1.210507000	-1.880219000
H	3.363366000	0.148387000	-2.077991000
C	3.163319000	1.730218000	-0.650655000
C	3.386189000	3.111651000	-0.343790000
H	2.500936000	0.066269000	0.015682000
H	-0.058705000	3.563990000	5.581311000

14 [V(MeO)L_3]

N	0.047668000	-0.001851000	-0.026014000
C	-1.101249000	-0.939660000	-0.196557000
H	-1.519526000	-1.175871000	0.800754000
H	-0.687783000	-1.866382000	-0.623558000
O	-0.523514000	-0.107378000	-2.761942000
C	-2.164322000	-0.377673000	-1.081950000
C	-1.819047000	0.020114000	-2.375605000
C	-2.784892000	0.520801000	-3.273241000
C	-4.088342000	0.594781000	-2.790601000
H	-4.860052000	0.974856000	-3.456615000
C	-4.479291000	0.214047000	-1.501152000
C	-3.485616000	-0.270415000	-0.658743000
H	-3.726020000	-0.588553000	0.355856000
C	-2.416916000	0.956008000	-4.691189000
C	-3.644117000	1.449909000	-5.472224000
H	-3.323240000	1.740872000	-6.483871000
H	-4.409010000	0.662914000	-5.569262000
H	-4.104478000	2.328841000	-4.993120000
C	-1.811438000	-0.233236000	-5.468001000
H	-1.559169000	0.093826000	-6.489924000
H	-0.899226000	-0.598312000	-4.979970000
H	-2.539493000	-1.057307000	-5.535858000
C	-5.941590000	0.347086000	-1.087514000
C	-6.178191000	-0.117238000	0.355238000
H	-7.243811000	-0.003180000	0.606723000
H	-5.905587000	-1.176536000	0.484229000
H	-5.590071000	0.480953000	1.069306000
C	-6.817929000	-0.506860000	-2.027008000
H	-7.879464000	-0.401975000	-1.749628000
H	-6.699140000	-0.186534000	-3.073067000
H	-6.537543000	-1.569369000	-1.957952000
O	1.691615000	1.877298000	-1.105991000
C	-0.460343000	1.273522000	0.565594000
H	-1.092154000	1.033660000	1.442600000
H	-1.112071000	1.725367000	-0.200408000
C	0.628899000	2.213194000	0.977885000
C	1.679859000	2.482197000	0.098937000
C	2.722470000	3.368084000	0.446572000
C	2.631064000	3.966974000	1.698399000
H	3.416442000	4.659776000	1.994420000
C	1.590084000	3.737374000	2.607274000
C	0.600193000	2.841237000	2.220306000
H	-0.228080000	2.612064000	2.891071000
C	3.893410000	3.620867000	-0.501561000
C	3.387106000	4.182641000	-1.848354000
H	4.250032000	4.367490000	-2.509304000
H	2.704852000	3.481800000	-2.345039000
H	2.862466000	5.138191000	-1.690189000
C	4.892814000	4.632119000	0.078356000
H	5.710213000	4.777180000	-0.644307000
H	4.418516000	5.609620000	0.260647000
H	5.331094000	4.273897000	1.023365000
C	4.651430000	2.295178000	-0.739432000
H	5.477470000	2.468320000	-1.448880000
H	5.078487000	1.925497000	0.206312000
H	3.989980000	1.524136000	-1.153609000
C	1.594386000	4.454599000	3.953658000
C	0.383621000	4.074296000	4.815331000
H	0.429865000	4.617164000	5.771857000
H	-0.561638000	4.337889000	4.315118000
H	0.370796000	2.994549000	5.033107000
C	1.569674000	5.979242000	3.719746000
H	1.594041000	6.508512000	4.686268000
H	2.439589000	6.299253000	3.126637000
H	0.656766000	6.272626000	3.178563000
C	2.878711000	4.089480000	4.726114000
H	2.899788000	4.619618000	5.692140000
H	2.920707000	3.005737000	4.916535000
H	3.775130000	4.374104000	4.154844000

O	1.798161000	0.954824000	-3.591421000
C	3.163328000	0.865153000	-3.955314000
H	3.258492000	0.993542000	-5.047568000
H	3.741235000	1.661521000	-3.450184000
H	3.583195000	-0.114083000	-3.664357000
V	1.056623000	0.428951000	-2.014617000
C	-1.393927000	2.112174000	-4.642117000
H	-1.200753000	2.464688000	-5.668551000
H	-1.794860000	2.955622000	-4.057306000
H	-0.437676000	1.790626000	-4.211396000
C	-6.375473000	1.822624000	-1.204805000
H	-7.437503000	1.925058000	-0.928515000
H	-5.773325000	2.457262000	-0.536020000
H	-6.247870000	2.188611000	-2.234620000
O	2.122167000	-1.040102000	-1.705960000
C	1.066690000	-0.619651000	0.874685000
H	0.651276000	-0.693419000	1.897492000
H	1.921591000	0.073028000	0.900814000
C	1.484630000	-1.971848000	0.393647000
C	2.004901000	-2.123612000	-0.895969000
C	2.407762000	-3.393989000	-1.369503000
C	2.261599000	-4.460433000	-0.489356000
H	2.562028000	-5.449537000	-0.828424000
C	1.752537000	-4.350350000	0.810156000
C	1.364738000	-3.083608000	1.224005000
H	0.961550000	-2.931075000	2.225300000
C	2.991485000	-3.579446000	-2.769862000
C	2.003893000	-3.074178000	-3.845404000
H	2.433372000	-3.261109000	-4.843130000
H	1.049573000	-3.619171000	-3.772137000
H	1.802624000	-2.001559000	-3.745477000
C	3.289821000	-5.054499000	-3.080490000
H	3.698557000	-5.124107000	-4.100092000
H	4.035221000	-5.474509000	-2.386633000
H	2.378307000	-5.671248000	-3.032703000
C	4.325462000	-2.807407000	-2.863749000
H	4.712145000	-2.859098000	-3.894789000
H	4.191437000	-1.755077000	-2.585425000
H	5.071171000	-3.256671000	-2.188706000
C	1.644917000	-5.593962000	1.686253000
C	1.066796000	-5.276305000	3.071105000
H	1.010227000	-6.201107000	3.665525000
H	1.700389000	-4.556614000	3.613177000
H	0.052212000	-4.854325000	2.993764000
C	0.730505000	-6.628201000	0.998213000
H	0.664223000	-7.539816000	1.614066000
H	-0.282649000	-6.218937000	0.862048000
H	1.125992000	-6.905481000	0.009452000
C	3.046503000	-6.211751000	1.870239000
H	2.977696000	-7.123508000	2.485679000
H	3.487088000	-6.481316000	0.898569000
H	3.721073000	-5.498377000	2.368659000

15 $[V(acac)_3]$

V	-0.096022000	0.001320000	0.000741000
C	1.978985000	1.847603000	0.976724000
C	3.052126000	2.098631000	2.005254000
H	2.586285000	2.205219000	2.997972000
H	3.636901000	2.999929000	1.776642000
H	3.722954000	1.226291000	2.054394000
C	1.795541000	2.737366000	-0.088980000
H	2.453217000	3.604154000	-0.147349000
C	0.771321000	2.621155000	-1.050711000
C	0.615569000	3.671937000	-2.121898000
H	0.684412000	3.193454000	-3.111685000
H	1.378098000	4.458459000	-2.040665000
H	-0.386585000	4.123373000	-2.048648000
C	-2.820390000	0.670538000	1.042902000
C	-3.618613000	1.372950000	2.114318000
H	-3.360597000	0.947074000	3.096786000
H	-4.700491000	1.282950000	1.947156000
H	-3.336176000	2.437415000	2.137463000
C	-3.481641000	-0.001504000	0.000703000
H	-4.570767000	-0.002654000	0.000877000
C	-2.819309000	-0.671722000	-1.041941000
C	-3.616358000	-1.375371000	-2.113425000
H	-3.359605000	-0.948470000	-3.095780000
H	-4.698378000	-1.287834000	-1.945865000
H	-3.331588000	-2.439203000	-2.137176000
C	0.769540000	-2.620011000	1.050456000
C	0.612716000	-3.671640000	2.120664000
H	0.682568000	-3.194273000	3.110917000
H	1.374116000	-4.459144000	2.038356000
H	-0.390088000	-4.121618000	2.047305000
C	1.793130000	-2.736817000	0.088162000
H	2.449491000	-3.604681000	0.145355000
C	1.977755000	-1.846028000	-0.976506000
C	3.050319000	-2.097516000	-2.005542000
H	2.584095000	-2.202330000	-2.998271000
H	3.633786000	-2.999947000	-1.778055000
H	3.722452000	-1.226139000	-2.053885000
O	1.262113000	0.788510000	1.176040000
O	-0.087047000	1.665811000	-1.074989000
O	-1.545106000	0.744910000	1.165012000
O	-1.543889000	-0.743192000	-1.164606000
O	-0.087374000	-1.663371000	1.076165000
O	1.262537000	-0.785585000	-1.174385000

16 $[V(MeOH)L_3]$

V	0.113560000	-0.072295000	0.126045000
N	0.069305000	0.428896000	2.180979000
O	0.189694000	-0.813639000	-1.901328000
H	-0.451652000	-1.542344000	-2.000325000
C	0.101564000	0.109832000	-3.013434000
H	-0.857719000	0.647225000	-2.998012000
H	0.241791000	-0.430774000	-3.961854000
H	0.922191000	0.822444000	-2.865592000
C	0.932345000	1.628987000	2.419675000
H	0.827101000	1.936495000	3.477146000
H	0.513437000	2.428253000	1.787372000
C	2.375495000	1.386284000	2.100963000
C	2.753439000	0.949109000	0.823275000
O	1.803383000	0.691977000	-0.107971000
C	4.119034000	0.767302000	0.501402000
C	5.043395000	1.041958000	1.503593000
H	6.100307000	0.912364000	1.278227000
C	4.705993000	1.474087000	2.791955000

C	3.353614000	1.634440000	3.062699000
H	3.025618000	1.970951000	4.046799000
C	4.548954000	0.282471000	-0.884157000
C	3.949049000	-1.113515000	-1.164178000
H	4.297302000	-1.835740000	-0.408802000
H	4.284407000	-1.460526000	-2.155782000
H	2.852616000	-1.085968000	-1.151694000
C	6.075731000	0.164128000	-1.005393000
H	6.572405000	1.133859000	-0.842302000
H	6.324413000	-0.181894000	-2.020424000
H	6.484398000	-0.563191000	-0.286025000
C	4.072949000	1.277677000	-1.964711000
H	4.532103000	2.266005000	-1.804192000
H	2.981232000	1.385275000	-1.936778000
H	4.375891000	0.909912000	-2.959184000
C	5.808255000	1.739393000	3.812584000
C	5.246168000	2.201770000	5.162956000
H	6.076054000	2.380272000	5.864015000
H	4.582665000	1.439529000	5.601290000
H	4.675539000	3.138082000	5.058533000
C	6.752002000	2.834618000	3.274748000
H	7.198986000	2.530439000	2.316283000
H	7.565710000	3.018550000	3.995319000
H	6.201194000	3.774568000	3.115049000
C	6.621386000	0.448065000	4.037703000
H	7.065766000	0.095397000	3.094791000
H	5.975442000	-0.350816000	4.434087000
H	7.435251000	0.635297000	4.757226000
C	-1.345504000	0.724661000	2.572503000
H	-1.391366000	0.855320000	3.669896000
H	-1.922531000	-0.178094000	2.314488000
C	-1.902338000	1.936895000	1.892986000
C	-1.887680000	2.038483000	0.494695000
O	-1.345475000	1.040783000	-0.248547000
C	-2.439733000	3.175909000	-0.142988000
C	-2.998959000	4.151372000	0.674944000
H	-3.434440000	5.030087000	0.202769000
C	-3.038137000	4.081539000	2.072312000
C	-2.469540000	2.957428000	2.655169000
H	-2.460977000	2.844921000	3.739769000
C	-2.390190000	3.333874000	-1.662367000
C	-3.127320000	2.162988000	-2.347949000
H	-2.720301000	1.196592000	-2.026093000
H	-3.028312000	2.257479000	-3.442459000
H	-4.199069000	2.191727000	-2.095159000
C	-3.058881000	4.632115000	-2.138603000
H	-2.558639000	5.521619000	-1.724426000
H	-4.123394000	4.665653000	-1.857452000
H	-2.992432000	4.683154000	-3.236466000
C	-0.912871000	3.384196000	-2.112574000
H	-0.355278000	2.513643000	-1.748330000
H	-0.433230000	4.295084000	-1.721392000
H	-0.860186000	3.410021000	-3.214050000
C	-3.677289000	5.214493000	2.868627000
C	-2.937319000	6.534311000	2.569036000
H	-3.406392000	7.363670000	3.123297000
H	-2.974952000	6.769875000	1.494735000
H	-1.880391000	6.461333000	2.869209000
C	-3.624242000	4.959210000	4.380285000
H	-4.161101000	4.035682000	4.648683000
H	-4.097883000	5.799557000	4.910835000
H	-2.584839000	4.870282000	4.733933000
C	-5.153892000	5.365213000	2.448607000
H	-5.712067000	4.439910000	2.659787000
H	-5.234780000	5.577981000	1.371912000
H	-5.620944000	6.195382000	3.003354000
C	0.584902000	-0.733461000	2.974842000
H	0.687414000	-0.422085000	4.031388000
H	1.593449000	-0.940041000	2.580890000
C	-0.297949000	-1.941376000	2.886946000
C	-0.640139000	-2.477650000	1.632587000
O	-0.175901000	-1.886707000	0.507376000
C	-1.455354000	-3.623806000	1.540557000
C	-1.887155000	-4.195338000	2.739498000
H	-2.511962000	-5.082212000	2.683781000

C	-1.568216000	-3.695379000	4.001578000
C	-0.770996000	-2.551879000	4.041081000
H	-0.499189000	-2.118718000	5.006482000
C	-1.854027000	-4.201700000	0.181212000
C	-0.596491000	-4.618423000	-0.612659000
H	0.080992000	-3.767055000	-0.757315000
H	-0.899597000	-5.017383000	-1.595394000
H	-0.051909000	-5.408929000	-0.072848000
C	-2.744343000	-5.445924000	0.317198000
H	-3.681914000	-5.218552000	0.848491000
H	-2.226620000	-6.255392000	0.855337000
H	-2.999888000	-5.812364000	-0.689110000
C	-2.655052000	-3.149943000	-0.619414000
H	-3.607092000	-2.926448000	-0.113085000
H	-2.881391000	-3.544452000	-1.624185000
H	-2.094162000	-2.209603000	-0.712576000
C	-2.052088000	-4.330242000	5.302308000
C	-2.919616000	-5.571613000	5.057508000
H	-3.239229000	-5.990076000	6.024364000
H	-2.361070000	-6.349215000	4.513236000
H	-3.820707000	-5.322404000	4.475355000
C	-2.885389000	-3.302558000	6.095738000
H	-3.221101000	-3.743542000	7.048591000
H	-3.770411000	-2.994630000	5.517408000
H	-2.290644000	-2.404079000	6.320408000
C	-0.834027000	-4.746351000	6.152536000
H	-1.171346000	-5.186477000	7.105234000
H	-0.196844000	-3.877681000	6.377764000
H	-0.224767000	-5.489762000	5.615452000