Supporting Information for:

DFT Analysis of Interligand Vibrations in Hydroperoxo Complex of Cobalt Bleomycin

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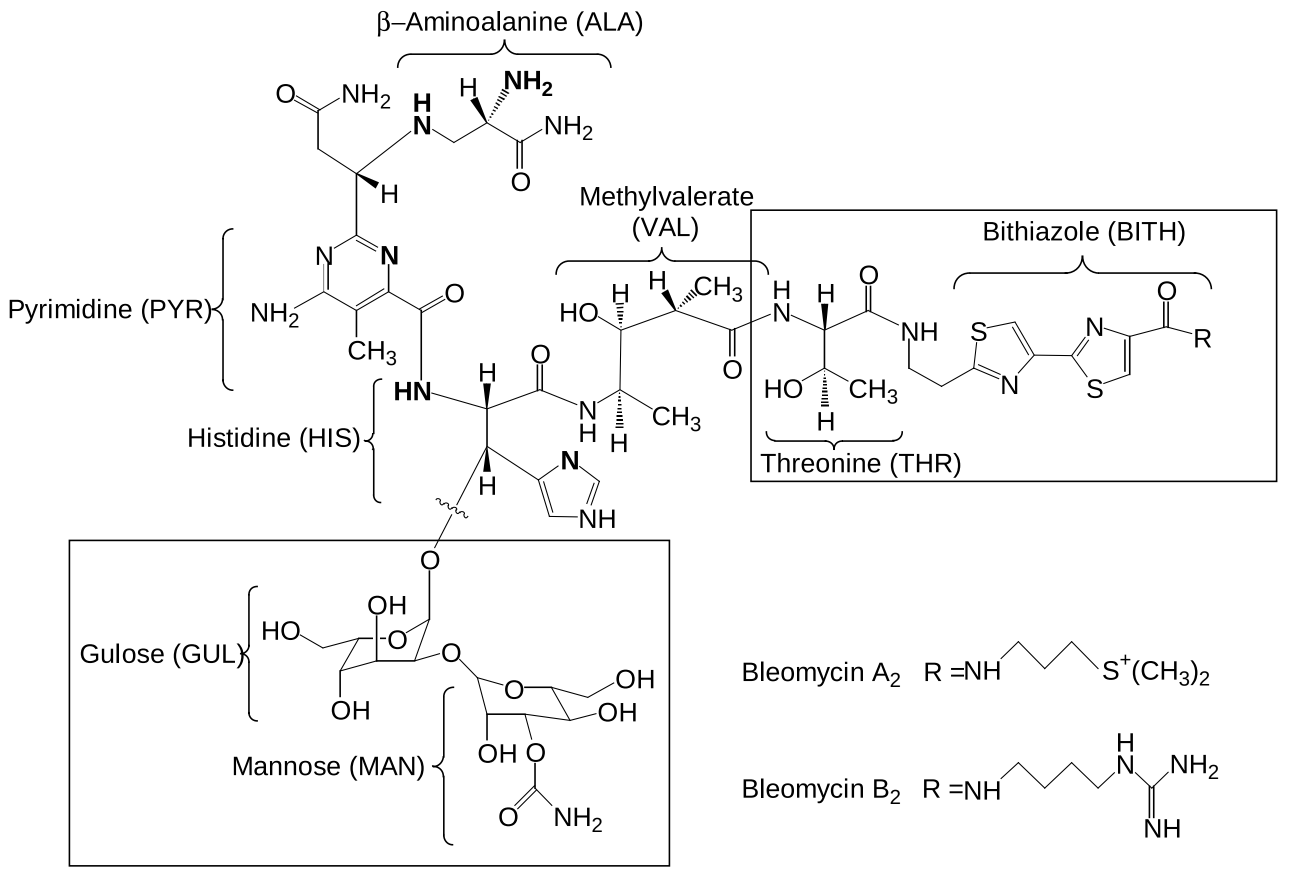

Figure SF1. Molecular structure of bleomycin. Boxed fragments have been truncated in calculations.

Table ST1. Bond Lengths (Å) and Angles (º) of optimized structures. All reported calculations were carried out within the GAUSSIAN 03[1] suite of programs for electronic structure calculations employing the B3LYP/6-31G(d) and BP86/6-31G(d) level of theory.

Parameters	B3LYP/6-31G(d)		BP86/6-31G(d)	
Å / º	'UP' conformer[a]	'DOWN' conformer[b]	'UP' conformer[c]	'DOWN' conformer[d]
Co-N_{HIS-I}	1.928	1.916	1.902	1.890
Co-N_{HIS-A}	1.953	1.955	1.929	1.931
Co-N_{PYR}	1.853	1.859	1.833	1.837
Co-$N_{A''-ALA}$	1.953	1.960	1.954	1.955
Co-$N_{A'-ALA}$	2.048	2.030	2.036	2.017
Co-OOH	1.874	1.880	1.884	1.897
O-OH	1.440	1.441	1.447	1.446
OO-H	0.977	0.981	0.993	0.998
$\angle N_{HIS-I}$-Co-N_{PYR}	175.18	177.50	175.59	178.02
$\angle O_{OOH}$-Co-$N_{A'-ALA}$	174.01	174.02	174.16	174.29
$\angle N_{HIS-A}$-Co-$N_{A''-ALA}$	165.60	166.52	166.42	167.46
$\angle N_{HIS-I}$-Co-N_{HIS-A}	94.89	95.79	95.53	96.17
$\angle N_{HIS-A}$-Co-N_{PYR}	82.45	81.84	82.89	82.27
$\angle N_{PYR}$-Co-$N_{A''-ALA}$	85.00	85.52	85.18	85.82
$\angle N_{A''-ALA}$-Co-N_{HIS-I}	98.11	96.91	96.82	95.82
$\angle N_{A'-ALA}$-Co-$N_{A''-ALA}$	85.74	86.60	86.25	87.00
$\angle N_{A'-ALA}$-Co-N_{HIS-A}	87.80	88.70	87.78	89.03
$\angle N_{A'-ALA}$-Co-N_{PYR}	92.54	89.89	92.48	89.81
$\angle N_{A'-ALA}$-Co-N_{HIS-I}	91.36	90.85	91.58	91.39
$\angle O_{OH}$-Co-$N_{A''-ALA}$	92.39	93.34	92.15	92.57
$\angle O_{OH}$-Co-N_{HIS-A}	92.72	90.02	92.58	90.20
$\angle O_{OH}$-Co-N_{PYR}	81.62	84.15	81.78	84.48
$\angle O_{OH}$-Co-N_{HIS-I}	94.53	95.10	94.19	94.31
∠O-O-H	101.03	101.28	100.64	100.93
∠Co-O-O_H	115.11	116.87	115.30	117.38
φCo-O-O-H	76.35	84.67	73.00	82.34

[a] -3445.502479 a.u.
[b] -3445.504772 a.u. ('Down' – 'Up') = 1.44 kcal/mol
[c] -3445.761637 a.u.
[d] -3445.764839 a.u. ('Down' – 'Up') = 2.01 kcal/mol

[1] M. J. Frisch et al., Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.

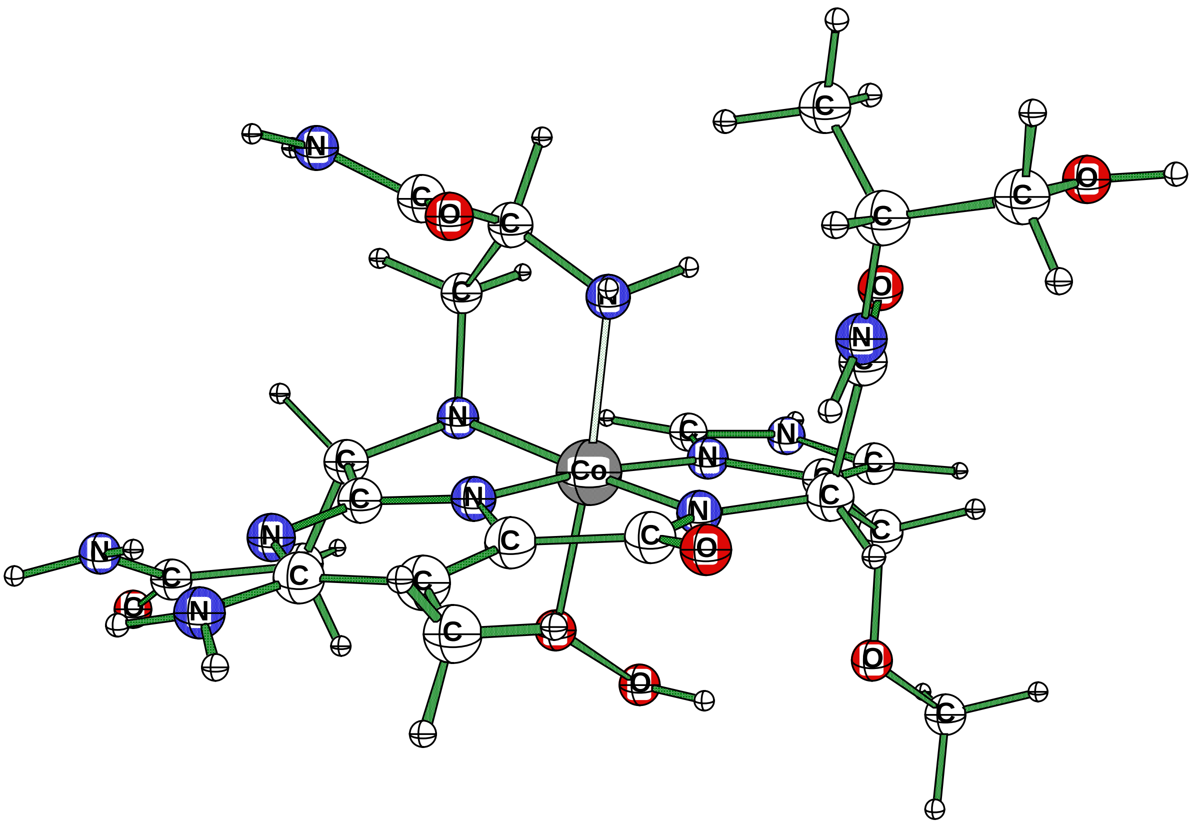

Figure SF2. B3LYP/6-31G(d) optimized structure of ‘up’ BLM-Co^{III}-OOH isomer

	X	Y	Z
Co	0.775277	0.081239	-0.315513
N	1.092240	1.294404	-1.812478
N	-0.009770	-1.088983	1.042989
H	3.375613	1.806428	-0.603170
C	0.365060	-1.135595	2.448353
O	-1.945527	-2.306732	1.455967
H	-0.113546	1.641547	-3.531284
C	0.751532	2.646369	-1.428898
N	2.328895	0.532559	0.734105
N	-0.677459	-0.501828	-1.306476
C	-2.467654	-1.620847	-2.916986
C	-1.477829	-1.449703	-0.769861
C	-0.718347	-0.180140	-2.594665
N	-1.608953	-0.716917	-3.429352
C	-2.448290	-2.050333	-1.554724
C	-1.163059	-1.683678	0.699063
C	0.377745	0.806491	-3.007442
C	1.888540	-1.096834	2.650948
H	0.034979	-2.093602	2.867810
H	2.078187	-1.027917	3.731904
H	4.435310	0.431791	3.263177
C	2.648327	0.018346	1.978320
C	3.313628	1.324222	0.360370
N	4.258506	1.374108	1.330221

C	3.853498	0.552606	2.362853
H	5.117360	1.902106	1.287708
H	1.599978	3.094953	-0.888537
C	-0.447768	2.745352	-0.437656
H	0.593811	3.296701	-2.306293
H	-0.410166	3.710243	0.091176
C	-1.862317	2.655889	-1.033875
O	-2.722291	1.928398	-0.544468
N	-2.123349	3.490943	-2.076293
H	-1.385326	3.961198	-2.577859
H	-3.027792	3.415094	-2.521298
C	-3.413215	-3.096713	-1.064046
H	-3.266173	-4.051532	-1.590079
H	-3.269796	-3.262597	0.003599
H	-4.451541	-2.780884	-1.234669
N	-3.402665	-2.116753	-3.780138
H	-3.886249	-2.969845	-3.544668
H	-3.248642	-1.940137	-4.762900
C	1.387722	0.160655	-4.009972
H	2.343959	0.657640	-3.839621
H	1.546584	-0.891313	-3.746772
C	1.100404	0.286156	-5.504947
O	2.005237	0.436355	-6.318476
N	-0.216944	0.246444	-5.885519
H	-0.381842	0.192037	-6.882025
H	-0.922325	-0.120224	-5.250234
O	2.353124	-2.379273	2.187337
C	-0.338391	0.008031	3.222962
O	0.239698	1.065618	3.488706
N	-1.637831	-0.283122	3.487281
H	-1.969030	-1.151771	3.062854
C	-2.644891	0.561952	4.144603
H	-3.607668	0.166938	3.794765
C	-2.574462	2.044013	3.756120
H	-2.650098	2.157541	2.669177
H	-3.419561	2.575350	4.209406
H	-1.643829	2.493627	4.100147
C	-2.645829	0.349898	5.664402
H	-3.547747	0.834268	6.077430
H	-2.722809	-0.730242	5.867970
O	-1.463320	0.897790	6.221103
H	-1.456920	0.695779	7.168404
N	-0.290979	1.623244	0.510051
H	0.136781	1.912982	1.390670
H	-1.230673	1.287552	0.739374
O	2.857535	-1.773205	-0.631446
H	2.550609	-2.269672	0.152443
O	1.603196	-1.349528	-1.197773
C	3.618454	-2.775057	2.685005
H	3.628350	-2.777455	3.786293
H	3.789001	-3.792347	2.324535
H	4.428544	-2.128226	2.321539

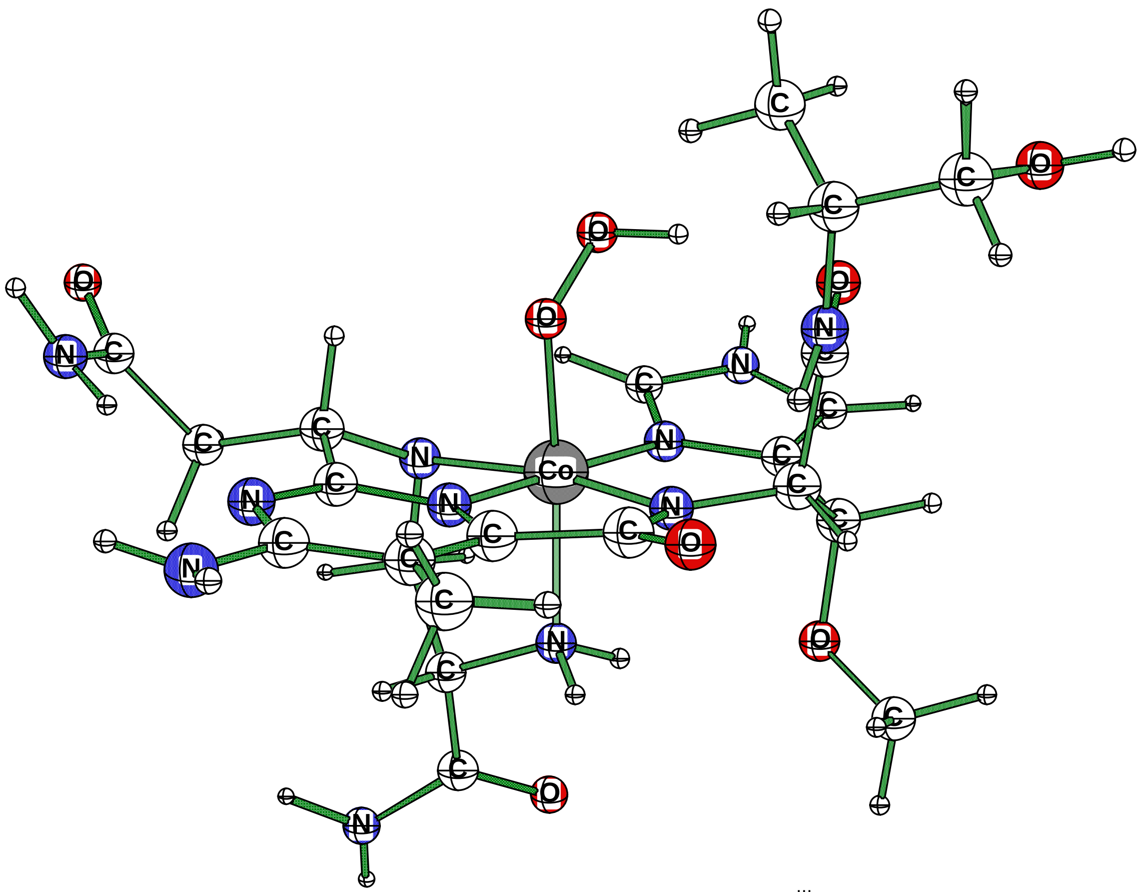

Figure SF3: B3LYP/6-31G(d) optimized structure of 'down' BLM-Co^{III}-OOH isomer

	X	Y	Z
N	0.807754	1.190123	-1.991740
Co	0.537545	0.257629	-0.294445
N	0.026245	-0.969360	1.145497
H	2.322153	2.807574	-0.510435
C	0.556876	-0.912194	2.496690
O	-1.676962	-2.423061	1.771719
H	-1.055061	2.019475	-2.145949
C	1.883314	0.532418	-2.706475
N	2.009680	1.050493	0.640965
N	-0.919225	-0.538531	-1.130973
C	-3.039930	-1.547807	-2.366346
C	-1.612734	-1.491925	-0.471784
C	-1.323753	-0.031615	-2.294398
N	-2.380860	-0.519659	-2.944194
C	-2.719069	-2.071397	-1.076632
C	-1.076573	-1.701362	0.939123
C	-0.508858	1.218461	-2.665669
C	2.085273	-0.660574	2.496368
H	0.380413	-1.876853	2.989426
H	2.416884	-0.639222	3.545480

H	4.026421	1.596586	3.184099
C	2.514515	0.624695	1.853797
C	2.568554	2.210912	0.354315
N	3.448682	2.540741	1.328010
C	3.427876	1.547211	2.288473
H	3.990555	3.391289	1.362700
H	1.890993	0.756111	-3.782394
C	1.906586	-1.014623	-2.491219
H	2.840574	0.903174	-2.309579
H	1.048703	-1.472189	-2.995633
C	3.210800	-1.636747	-2.980282
O	4.155159	-1.831798	-2.223660
N	3.263150	-1.922227	-4.316191
H	2.545205	-1.603718	-4.950648
H	4.163102	-2.165000	-4.708378
C	-3.554009	-3.163270	-0.460609
H	-3.531094	-4.072459	-1.077577
H	-3.180630	-3.397985	0.536213
H	-4.605502	-2.854142	-0.368521
N	-4.056698	-2.090971	-3.094894
H	-4.734383	-2.685489	-2.643729
H	-4.359027	-1.585122	-3.915233
C	-0.466792	1.563659	-4.176755
H	0.428271	2.161477	-4.356381
H	-0.406955	0.652945	-4.787655
C	-1.624346	2.438534	-4.672298
O	-1.454791	3.603817	-5.005482
N	-2.839625	1.814390	-4.750134
H	-3.638987	2.411813	-4.913736
H	-2.972249	0.931559	-4.263745
O	2.779994	-1.708380	1.805783
C	-0.210221	0.170575	3.307843
O	0.270457	1.284754	3.527868
N	-1.439717	-0.251423	3.688160
H	-1.712333	-1.160479	3.313379
C	-2.503706	0.541091	4.322635
H	-3.438250	0.105926	3.943028
C	-2.495622	2.031043	3.956714
H	-2.403505	2.166356	2.875247
H	-3.441670	2.478354	4.285413
H	-1.670108	2.550349	4.441704
C	-2.527980	0.309432	5.839441
H	-3.445159	0.771340	6.243961
H	-2.586028	-0.774537	6.032184
O	-1.363662	0.872501	6.420391
H	-1.387390	0.692809	7.371787
N	1.750487	-1.191776	-1.036192
H	1.379739	-2.111561	-0.800617
H	2.677283	-1.166014	-0.600878
O	-0.735201	1.501344	0.312371
O	-0.230697	2.688717	0.954968
H	-0.111037	2.372544	1.875423
C	2.820390	-2.952603	2.481733
H	3.180894	-2.834472	3.515641
H	1.842606	-3.453722	2.506117
H	3.524792	-3.581950	1.931423

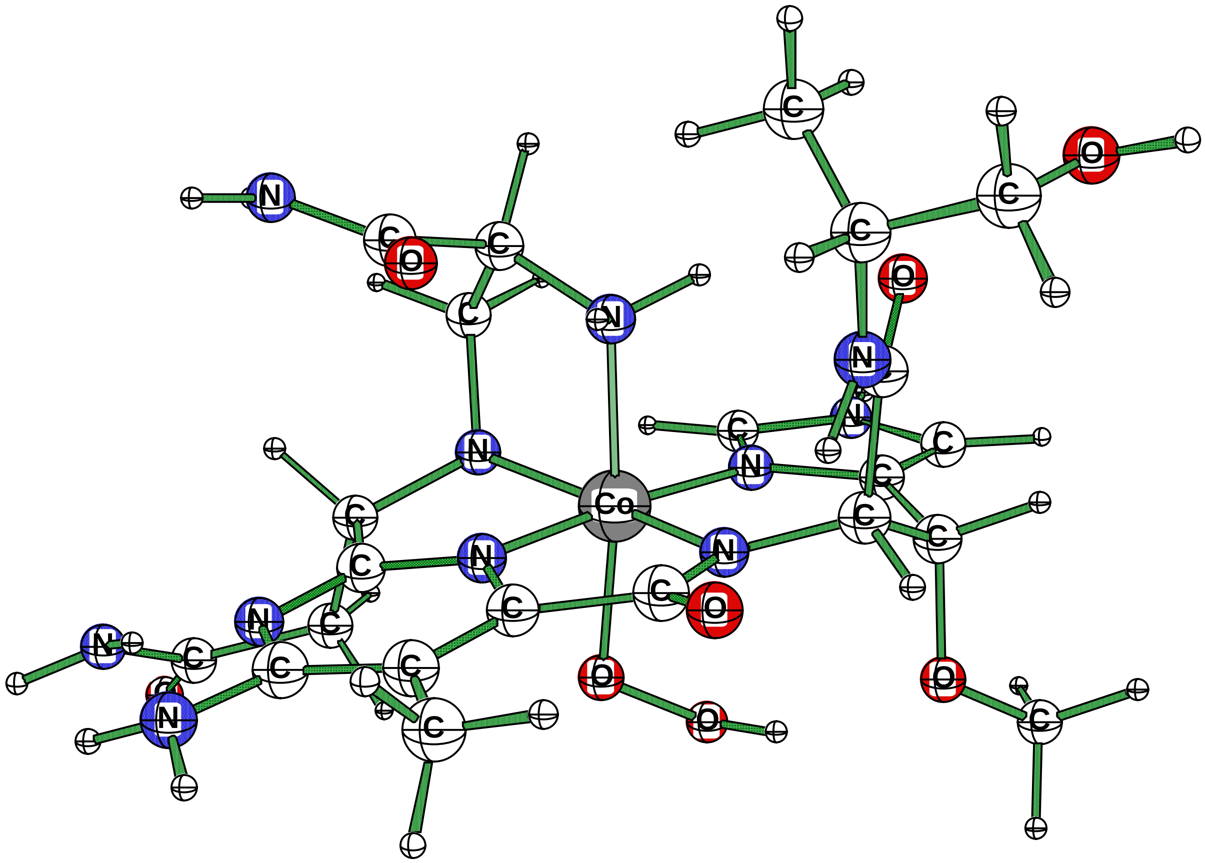

Figure SF4: BP86/6-31G(d) optimized structure of 'up' BLM-Co^{III}-OOH isomer

	X	Y	Z
Co	0.779355	0.076603	-0.307471
N	1.103995	1.298646	-1.796866
N	0.024181	-1.091780	1.028668
H	3.352383	1.794581	-0.688105
C	0.401559	-1.133576	2.438482
O	-1.921045	-2.322818	1.488593
H	-0.104012	1.676434	-3.528962
C	0.748684	2.649855	-1.396208
N	2.323954	0.536232	0.702657
N	-0.656255	-0.496714	-1.292778
C	-2.524627	-1.560786	-2.895398
C	-1.474022	-1.449039	-0.753951
C	-0.724832	-0.152938	-2.589486
N	-1.647040	-0.663176	-3.419718
C	-2.485068	-2.012315	-1.537862
C	-1.149065	-1.695909	0.698416
C	0.378857	0.823514	-3.003566
C	1.927519	-1.080710	2.637502
H	0.070351	-2.104759	2.855652
H	2.127509	-1.020519	3.727367

H	4.482021	0.500525	3.223522
C	2.666515	0.044515	1.958859
C	3.306107	1.339674	0.299885
N	4.268870	1.408044	1.264657
C	3.884611	0.596584	2.319849
H	5.129545	1.947413	1.203984
H	1.598849	3.098514	-0.838035
C	-0.460433	2.729773	-0.409036
H	0.595422	3.314342	-2.276899
H	-0.434944	3.697577	0.135335
C	-1.882618	2.619101	-1.000669
O	-2.746933	1.901521	-0.475796
N	-2.150902	3.429270	-2.070768
H	-1.399005	3.851671	-2.612081
H	-3.056652	3.317139	-2.525365
C	-3.461053	-3.043163	-1.028831
H	-3.336952	-4.012790	-1.553051
H	-3.296937	-3.204575	0.047743
H	-4.505886	-2.710639	-1.184905
N	-3.502549	-2.016653	-3.750401
H	-3.967803	-2.892442	-3.519977
H	-3.334507	-1.851437	-4.742304
C	1.395342	0.177501	-4.004642
H	2.344993	0.717026	-3.861296
H	1.596614	-0.864695	-3.695201
C	1.088482	0.236829	-5.506261
O	1.993736	0.323840	-6.345270
N	-0.244516	0.221718	-5.861090
H	-0.426898	0.119671	-6.860093
H	-0.951544	-0.117686	-5.191246
O	2.405932	-2.367887	2.153551
C	-0.315497	0.009157	3.218633
O	0.255844	1.082904	3.490207
N	-1.618070	-0.309439	3.474204
H	-1.930100	-1.188466	3.019642
C	-2.648790	0.521627	4.124411
H	-3.610382	0.108926	3.761504
C	-2.591212	2.010042	3.740984
H	-2.674851	2.128923	2.646566
H	-3.442629	2.538793	4.206471
H	-1.651934	2.464047	4.084855
C	-2.661074	0.302240	5.649308
H	-3.591064	0.765928	6.053320
H	-2.717185	-0.790912	5.847257
O	-1.491273	0.882074	6.220207
H	-1.494740	0.660227	7.172962
N	-0.288736	1.593933	0.529937
H	0.133520	1.880279	1.427002
H	-1.242338	1.250986	0.749910
O	2.886355	-1.772477	-0.642946
H	2.578196	-2.233578	0.180641
O	1.620421	-1.351276	-1.202923
C	3.697308	-2.726181	2.640208
H	3.712527	-2.751166	3.750722
H	3.904238	-3.736183	2.252465
H	4.486611	-2.033803	2.284042

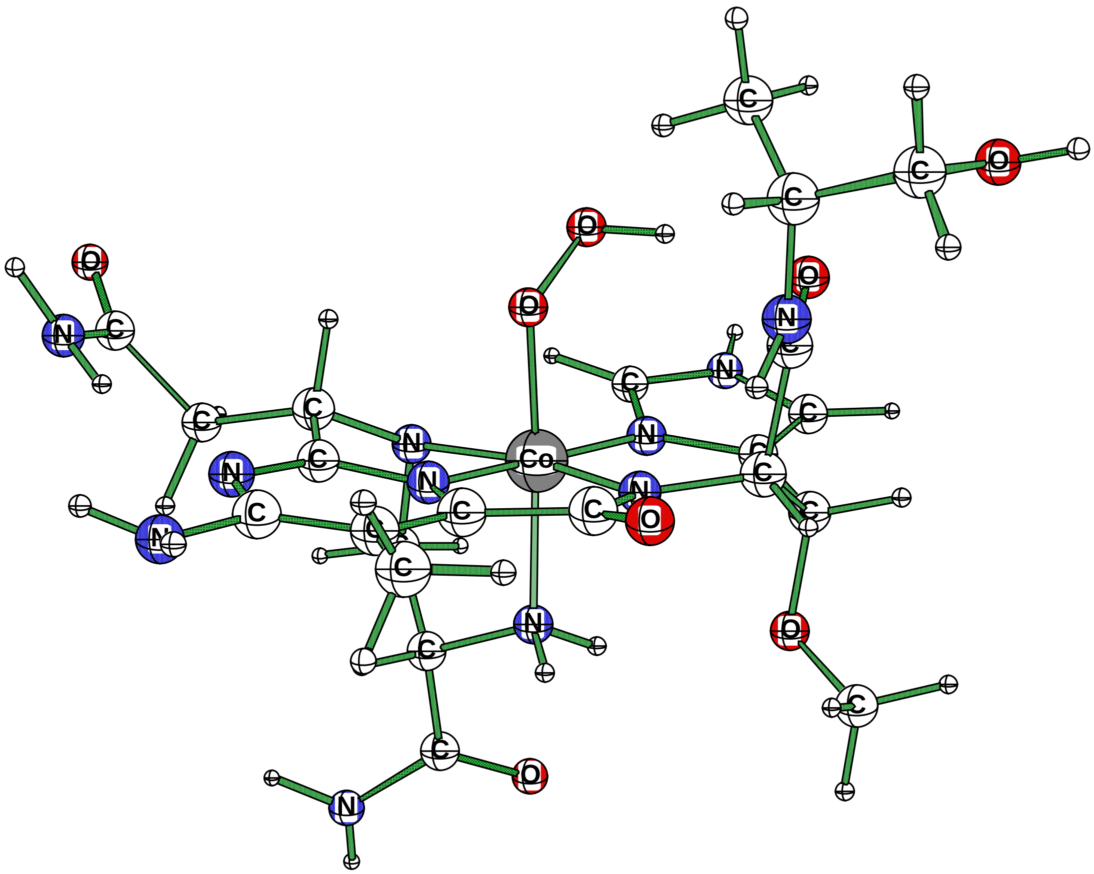

Figure SF5: BP86/6-31G(d) optimized structure of 'down' BLM-Co^{III}-OOH isomer

	X	Y	Z
N	0.810588	1.209320	-1.968839
Co	0.542237	0.251735	-0.285785
N	0.041539	-0.951075	1.139179
H	2.290124	2.800029	-0.569784
C	0.580398	-0.900383	2.491373
O	-1.660534	-2.424369	1.806240
H	-1.060111	2.050410	-2.100724
C	1.877898	0.543177	-2.699693
N	2.000135	1.044222	0.620105
N	-0.906202	-0.519304	-1.111032
C	-3.021026	-1.570794	-2.379235
C	-1.601890	-1.495507	-0.458324
C	-1.322152	-0.012052	-2.288439
N	-2.373329	-0.516049	-2.951053
C	-2.703766	-2.090059	-1.083341
C	-1.073286	-1.700716	0.944299
C	-0.517040	1.248076	-2.643957
C	2.113270	-0.653041	2.489427
H	0.394470	-1.875425	2.984763
H	2.447897	-0.625955	3.548792

H	4.093285	1.619922	3.126757
C	2.535006	0.628843	1.832260
C	2.560343	2.211910	0.305045
N	3.467754	2.548551	1.265192
C	3.468120	1.561628	2.239355
H	4.017848	3.404392	1.280421
H	1.882364	0.787980	-3.781297
C	1.876094	-1.014273	-2.505329
H	2.849915	0.893178	-2.293057
H	0.995097	-1.452598	-3.007210
C	3.174882	-1.653232	-2.997468
O	4.146611	-1.808261	-2.245375
N	3.201697	-1.998347	-4.329081
H	2.465184	-1.699846	-4.966266
H	4.106334	-2.238454	-4.734216
C	-3.522187	-3.195053	-0.462285
H	-3.461826	-4.124793	-1.061750
H	-3.154424	-3.396956	0.555789
H	-4.592910	-2.914018	-0.394263
N	-4.017032	-2.145269	-3.133629
H	-4.711536	-2.720631	-2.661842
H	-4.345634	-1.606028	-3.933793
C	-0.471935	1.622420	-4.150466
H	0.413884	2.257312	-4.309574
H	-0.374198	0.716349	-4.779948
C	-1.661429	2.471251	-4.641289
O	-1.533862	3.659080	-4.954276
N	-2.853528	1.790675	-4.738356
H	-3.684434	2.363518	-4.887319
H	-2.946565	0.890111	-4.246641
O	2.813194	-1.711963	1.798388
C	-0.195291	0.187904	3.300681
O	0.273180	1.324621	3.505120
N	-1.420099	-0.260480	3.691825
H	-1.675410	-1.183155	3.298328
C	-2.507981	0.519416	4.314197
H	-3.439441	0.072612	3.912813
C	-2.505288	2.016615	3.960972
H	-2.395424	2.164507	2.874129
H	-3.466931	2.457373	4.282386
H	-1.683735	2.539647	4.468371
C	-2.554143	0.273749	5.834585
H	-3.501296	0.713046	6.224864
H	-2.592346	-0.823451	6.017521
O	-1.406980	0.866156	6.438937
H	-1.447739	0.664171	7.395077
N	1.732045	-1.191803	-1.040011
H	1.350574	-2.118573	-0.803091
H	2.680375	-1.182057	-0.623136
O	-0.720560	1.524301	0.335541
O	-0.207146	2.697425	1.007747
H	-0.068542	2.341787	1.929493
C	2.814203	-2.959945	2.487527
H	3.157813	-2.841811	3.537833
H	1.819101	-3.449422	2.494785
H	3.524825	-3.608630	1.949923