Supporting Information

Theoretical Rationalization for the Equilibrium between (μ-η^2:η^2-Peroxido)$Cu^{II}Cu^{II}$ and Bis(μ-oxido)$Cu^{III}Cu^{III}$ Complexes: Perturbational Effects from Ligand Frameworks

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Table of Contents

Fig. S1 Plots of the calculated energy differences between the (μ-η^2:η^2-peroxido)$Cu^{II}Cu^{II}$ **1** and the bis(μ-oxido)$Cu^{III}Cu^{III}$ complex **2** in **La** and **Lb** ligand systems along with the ratio of the Hartree–Fock exchange in the functionals with Grimme's dispersion correction (D3).

Fig. S2 Calculated energy differences between the (μ-η^2:η^2-peroxido)$Cu^{II}Cu^{II}$ **1** and the bis(μ-oxido)$Cu^{III}Cu^{III}$ complex **2** in (A) **La** and (B) **Lb** ligand systems using the B3LYP* functional without Grimme's dispersion correction (D3).

Fig. S3 (A) Schematic representation of the bonding and antibonding orbitals consisting of the d_{Ax2-y2} and d_{Bx2-y2} orbitals of the Cu^{II} ions and the lone pair orbitals of the N2 and N3 (N5 and N6) atoms in **1a**. (B) Walsh diagram of the bonding and antibonding orbitals consisting of the d_{Ax2-y2} and d_{Bx2-y2} orbitals of the Cu^{II} ions and the lone pair orbitals of the N2 and N3 (N5 and N6) atoms as a function of the N2–N3 (N5–N6) distance in **1a**.

Fig. S4 Plots of energy gaps between the σ* and d_{Ax2-y2} orbitals along the distance of the diamine framework N2–N3 (N5–N6) in **1a**.

Fig. S5 Plots of the O1–O2 bond distance along the distance of the diamine framework N2–N3 (N5–N6) in **1a**.

Fig. S6 Plots of Mayer bond order of the O1–O2 bond along the distance of the diamine framework N2–N3 (N5–N6) in **1a**.

Fig. S7 Plots of energy gaps between the $d_{Ax2-y2} - \sigma$* and $d_{x2-y2} + \sigma$* orbitals along the distance of the diamine framework N2–N3 (N5–N6) in **2a**.

Table S1 Cartesian coordinates of $[Cu^{II}_2(\mathbf{La})_2(O_2^{2-})]^{2+}$ (**1a**) in the open-shell singlet state.

Table S2 Cartesian coordinates of $[Cu^{III}_2(\mathbf{La})_2(O^{2-})_2]^{2+}$ (**2a**) in the closed-shell singlet state.

Table S3 Cartesian coordinates of $[Cu^{II}_2(\mathbf{Lb})_2(O_2^{2-})]^{2+}$ (**1b**) in the open-shell

singlet state.

Table S4 Cartesian coordinates of $[Cu^{III}_2(\mathbf{Lb})_2(O^{2-})_2]^{2+}$ (**2b**) in the closed-shell singlet state.

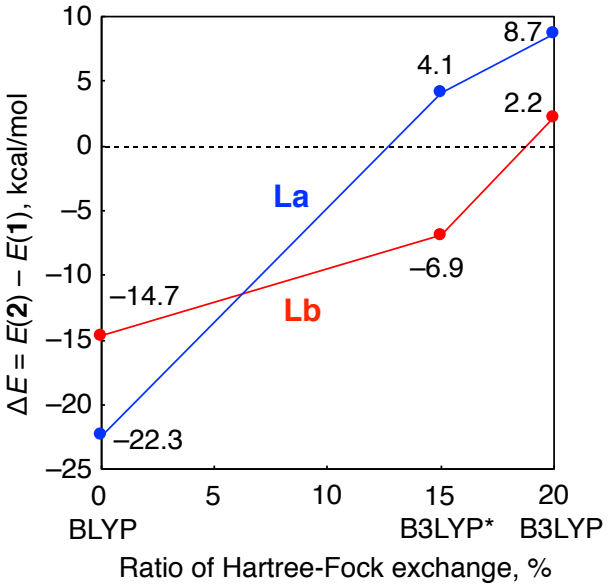

Fig. S1 Plots of the calculated energy differences between the (μ-η^2:η^2-peroxido)$Cu^{II}Cu^{II}$ **1** and the bis(μ-oxido)$Cu^{III}Cu^{III}$ complex **2** in **La** and **Lb** ligand systems along with the ratio of the Hartree–Fock exchange in the functionals with Grimme's dispersion correction (D3). A dotted line stands for the equal of the energies of **1** and **2**.

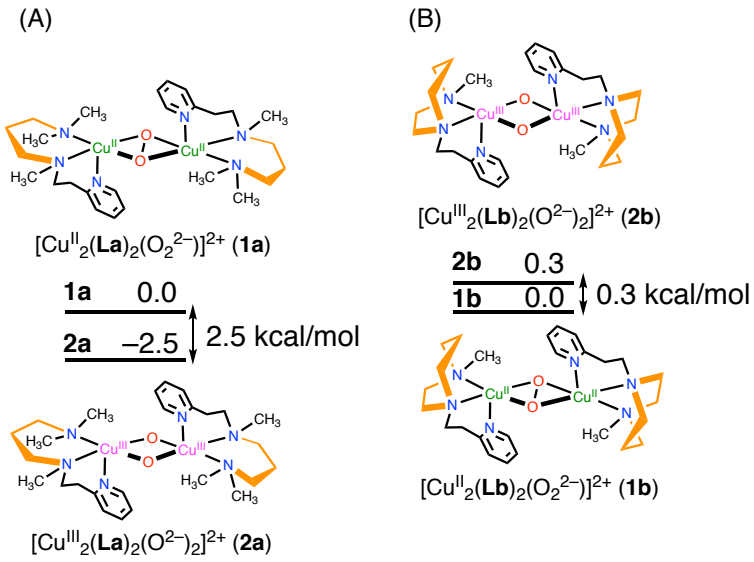

Fig. S2 Calculated energy differences between the (μ-η^2:η^2-peroxido)$Cu^{II}Cu^{II}$ **1** and the bis(μ-oxido)$Cu^{III}Cu^{III}$ complex **2** in (A) **La** and (B) **Lb** ligand systems using the B3LYP* functional without Grimmie's dispersion correction (D3).

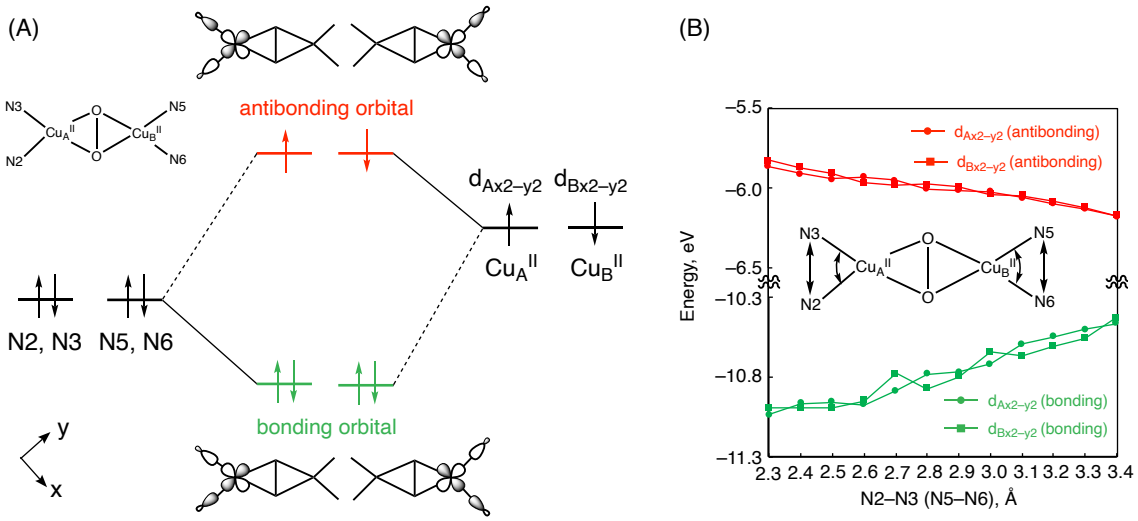

Fig. S3 (A) Schematic representation of the bonding and antibonding orbitals consisting of the d_{Ax2-y2} and d_{Bx2-y2} orbitals of the Cu^{II} ions and the lone pair orbitals of the N2 and N3 (N5 and N6) atoms in **1a**. (B) Walsh diagram of the bonding and antibonding orbitals consisting of the d_{Ax2-y2} and d_{Bx2-y2} orbitals of the Cu^{II} ions and the lone pair orbitals of the N2 and N3 (N5 and N6) atoms as a function of the N2–N3 (N5–N6) distance in **1a**.

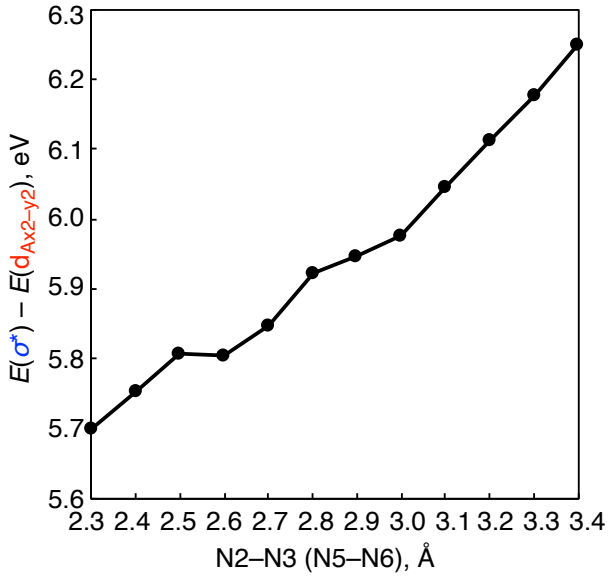

Fig. S4 Plots of energy gaps between the σ^* and d_{Ax2-y2} orbitals along the distance of the diamine framework N2–N3 (N5–N6) in **1a**.

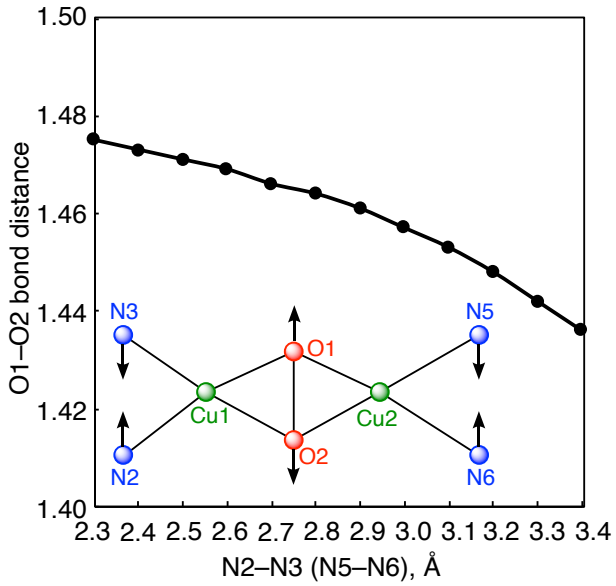

Fig. S5 Plots of the O1–O2 bond distance along the distance of the diamine framework N2–N3 (N5–N6) in **1a**.

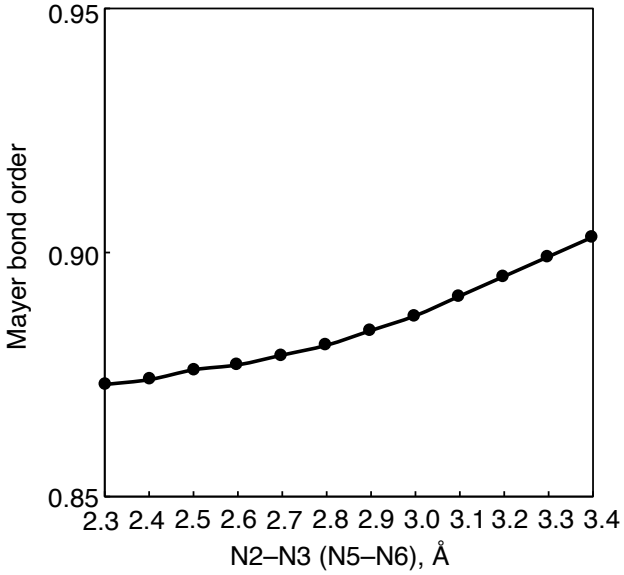

Fig. S6 Plots of Mayer bond order of the O1–O2 bond along the distance of the diamine framework N2–N3 (N5–N6) in **1a**.

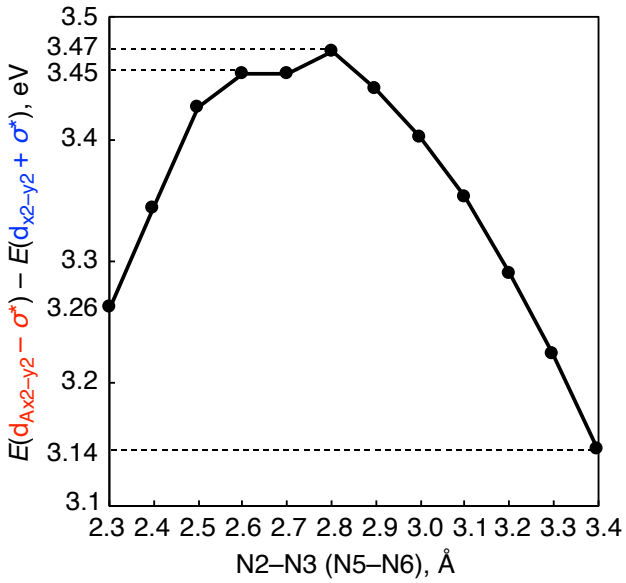

Fig. S7 Plots of the energy gaps between the $d_{Ax2-y2} - \sigma^*$ and $d_{x2-y2} + \sigma^*$ orbitals along the distance of the diamine framework N2–N3 (N5–N6) in **2a**.

Table S1 Cartesian coordinates of $[Cu^{II}_2(\mathbf{La})_2(O_2^{2-})]^{2+}$ (**1a**) in the open-shell singlet state.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	3.836724	-2.437300	1.085554
C	-2.473578	2.600847	-1.391218
C	4.583853	-2.516439	-0.250147
C	-2.792833	3.243597	-0.036815
H	4.549284	-2.589620	1.912764
H	-3.108032	3.053445	-2.170275
C	3.681758	-2.641636	-1.481703
C	-1.788678	2.932306	1.077386
H	5.305041	-1.698502	-0.362748
H	-3.820883	3.034114	0.280167
H	5.186392	-3.433480	-0.210319
H	-2.752661	4.329278	-0.196802
N	2.908850	-1.410941	-1.830212
N	-1.789876	1.518928	1.561436
H	4.289790	-2.931974	-2.354227
H	-1.978509	3.598228	1.935445
H	2.948487	-3.439422	-1.306598
H	-0.776191	3.144616	0.711467
C	3.812832	-0.337559	-2.317633
C	-3.039617	1.206495	2.300777
C	1.944431	-1.749428	-2.913010
C	-0.637467	1.337295	2.482077
N	3.078311	-1.169682	1.339751
N	-2.628541	1.111280	-1.460579
H	3.104994	-3.253822	1.123967
H	-1.431465	2.825919	-1.645528
H	3.214418	0.526773	-2.617945

H	-2.998062	0.171526	2.652561
H	4.492023	-0.017558	-1.524468
H	-3.907843	1.305151	1.645762
H	4.402592	-0.688202	-3.178459
H	-3.162362	1.881329	3.162118
H	1.377930	-0.854417	-3.187771
H	-0.643605	0.314939	2.870373
H	2.474720	-2.131598	-3.798957
H	-0.693039	2.047222	3.321795
H	1.239630	-2.501836	-2.548437
H	0.291677	1.492018	1.928525
C	2.239787	-1.381351	2.551897
C	-2.073248	0.646176	-2.762825
C	4.043664	-0.046315	1.558658
C	-4.084186	0.767833	-1.365281
H	1.615415	-0.505914	2.736368
H	-2.042147	-0.445248	-2.791234
H	1.574056	-2.231155	2.377625
H	-1.047364	1.010096	-2.861521
H	2.869576	-1.576092	3.433470
H	-2.674762	1.024435	-3.603391
C	3.444771	1.320402	1.919389
C	-4.455802	-0.713388	-1.511056
H	4.726510	-0.339990	2.372371
H	-4.613093	1.329557	-2.152137
H	4.641995	0.060570	0.649547
H	-4.452009	1.129787	-0.401578
H	4.278108	1.936929	2.277964
H	-5.540544	-0.744629	-1.667955
C	2.739368	2.087262	0.818983
C	-4.119619	-1.628894	-0.352494
H	2.765569	1.231381	2.778317
H	-4.015317	-1.132738	-2.425748

Cu	1.826692	-0.769302	-0.212355
Cu	-1.556413	0.193251	-0.008781
O	-0.023428	-0.866639	-0.874513
O	-0.012515	-0.843848	0.574810
N	2.083206	1.404306	-0.141543
N	-2.936630	-1.473729	0.279850
C	1.433808	2.089741	-1.104304
C	-2.601829	-2.340843	1.259550
C	1.388524	3.482683	-1.159117
C	-3.426913	-3.390176	1.669014
C	2.059355	4.202624	-0.156881
C	-4.666285	-3.546684	1.029199
C	2.742960	3.495126	0.837147
C	-5.011461	-2.655939	0.006791
H	3.279150	4.020184	1.626010
H	-5.961103	-2.750570	-0.517185
H	2.052848	5.291797	-0.155855
H	-5.347244	-4.346027	1.319723
H	0.852685	3.983746	-1.962691
H	-3.104432	-4.057933	2.465332
H	0.922256	1.477828	-1.845634
H	-1.624196	-2.180499	1.711825

Table S2 Cartesian coordinates of $[Cu^{III}_2(\mathbf{La})_2(O^{2-})_2]^{2+}$ (**2a**) in the closed-shell singlet state.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-3.648806	-1.133880	-1.355500
C	-4.298881	-1.665486	-0.081904
H	-4.424715	-0.930350	-2.108387
C	-3.300148	-2.261518	0.904375
H	-4.946780	-0.919256	0.391202
H	-4.962940	-2.484051	-0.387960
N	-2.355589	-1.285364	1.534216
H	-3.841753	-2.776759	1.711946
H	-2.681803	-3.005790	0.387278
C	-3.066540	-0.366950	2.466936
C	-1.380900	-2.080272	2.339670
N	-2.825809	0.111815	-1.197316
H	-2.981028	-1.902710	-1.763147
H	-2.344649	0.329726	2.897357
H	-3.827526	0.210875	1.943560
H	-3.545399	-0.949656	3.266912
H	-0.716424	-1.402444	2.878175
H	-1.930866	-2.707758	3.055558
H	-0.780240	-2.703950	1.674875
C	-2.244267	0.409674	-2.537080
C	-3.713585	1.250404	-0.766323
H	-1.541637	1.239799	-2.465732
H	-1.697684	-0.466902	-2.889839
H	-3.051133	0.654385	-3.242478
C	-3.138597	2.662099	-0.889629
H	-4.625414	1.198543	-1.379618

H	-3.998858	1.076806	0.271021
H	-3.972008	3.340856	-0.653527
C	-1.988605	3.009391	0.034844
H	-2.865603	2.895684	-1.925263
Cu	-1.327173	-0.217652	0.134312
O	0.231485	-0.462272	1.028892
O	-0.090549	0.494693	-0.992078
Cu	1.472361	0.182646	-0.131815
N	2.932121	-0.165660	1.202953
C	4.338931	0.027376	0.734167
C	4.574827	1.287398	-0.094268
C	3.950883	1.188212	-1.482646
N	2.458490	1.260700	-1.509022
C	2.002880	0.815235	-2.856776
C	1.987730	2.656841	-1.265629
C	2.782695	-1.546187	1.791985
H	2.461086	1.447367	-3.630347
H	0.914955	0.889372	-2.907719
H	2.388451	3.329269	-2.037402
H	0.895268	2.667837	-1.287534
H	2.319248	3.000080	-0.282227
H	4.235611	0.230413	-1.934267
H	4.335097	1.990530	-2.130111
H	5.659267	1.381313	-0.233044
H	4.259556	2.195371	0.433026
H	4.612867	-0.838207	0.125184
H	4.986553	0.029688	1.623346
N	-1.631000	2.113002	0.970230
C	-0.645216	2.437725	1.828241
C	0.035976	3.656696	1.796537
C	-0.323472	4.587884	0.807024
C	-1.348783	4.258097	-0.084555
H	-1.659245	4.952045	-0.864922

H	0.188120	5.547052	0.733265
H	0.824894	3.864585	2.517145
H	-0.376419	1.667081	2.549390
H	3.528431	-1.628764	2.597057
C	2.632428	0.812747	2.295084
H	2.687729	1.835411	1.913375
H	1.620415	0.626865	2.659060
H	3.353547	0.694711	3.115697
H	2.304608	-0.225660	-3.001347
H	1.785612	-1.587401	2.238422
C	2.960883	-2.741335	0.835554
H	3.117208	-3.615926	1.477925
H	3.871529	-2.632729	0.234621
C	-0.318273	-3.432247	-1.815299
C	-0.119093	-4.336165	-0.761398
C	0.954371	-4.121378	0.112968
C	1.792020	-3.009182	-0.085178
N	1.591099	-2.133125	-1.092715
C	0.562082	-2.350203	-1.931541
H	-1.126406	-3.561088	-2.533391
H	-0.783969	-5.188770	-0.625304
H	1.143344	-4.802191	0.941329
H	0.422727	-1.608945	-2.716455

Table S3 Cartesian coordinates of $[Cu^{II}_2(\mathbf{Lb})_2(O_2^{2-})]^{2+}$ (**1b**) in the open-shell singlet state.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-3.488067	-2.012367	-1.850960
C	-3.769855	-3.230683	-0.964204
H	-4.273197	-1.956130	-2.620357
C	-2.897203	-3.360161	0.289124
H	-4.828256	-3.238718	-0.677296
H	-3.616809	-4.128912	-1.575372
N	-2.856667	-2.106780	1.106435
H	-3.291855	-4.181524	0.908642
H	-1.860590	-3.603881	0.024008
C	-4.194352	-1.462720	1.214040
C	-2.267364	-2.393637	2.432683
N	-3.449425	-0.717865	-1.091506
H	-2.519840	-2.111076	-2.357566
H	-2.159025	-1.462562	2.998720
H	-2.893608	-3.095471	3.004957
H	-1.273181	-2.829288	2.286099
C	-4.538051	-0.642071	-0.068986
C	-3.504433	0.441015	-2.042685
C	-2.442107	1.529237	-1.778507
H	-3.329195	0.060255	-3.054230
H	-2.589175	2.322204	-2.520769
C	-2.442685	2.121166	-0.389252
H	-1.451555	1.085733	-1.955275
Cu	-1.764879	-0.739901	0.053048
O	0.082866	-1.106097	0.449700
O	0.038241	-0.817077	-0.981157
Cu	1.507007	0.200758	-0.264068

N	2.717261	1.301763	1.021072
C	1.988238	2.565872	1.379701
C	1.016166	3.030754	0.290073
C	1.555981	3.046569	-1.140205
N	2.077017	1.702403	-1.567814
C	1.728723	1.426342	-2.980711
C	3.169984	0.574657	2.252342
C	3.020835	-0.958406	2.159904
C	3.667976	-1.618012	0.963348
H	2.141181	2.195417	-3.651199
H	2.123127	0.447345	-3.271699
H	0.639016	1.403532	-3.081817
H	2.353197	3.793712	-1.264045
H	0.738377	3.324643	-1.813553
H	0.665373	4.039001	0.547505
H	0.135816	2.380113	0.308089
H	2.722893	3.349186	1.619135
H	1.402395	2.368667	2.283102
N	-2.060545	1.293484	0.614656
C	-1.987957	1.768316	1.872784
C	-2.286299	3.094157	2.200129
C	-2.686992	3.957159	1.169227
C	-2.767658	3.462298	-0.139946
H	-3.067884	4.106801	-0.963900
H	-2.926507	4.998601	1.380431
H	-2.202935	3.433307	3.230373
H	-1.668257	1.059196	2.635593
N	3.081612	-1.395907	-0.237933
C	3.576850	-2.009812	-1.328014
C	4.686520	-2.861696	-1.290260
C	5.313210	-3.076612	-0.053639
C	4.793508	-2.448315	1.086752
H	3.059490	-1.810892	-2.266999

H	5.042447	-3.335514	-2.202856
H	6.184482	-3.726370	0.021980
H	5.245502	-2.601758	2.065167
H	3.431870	-1.383479	3.083255
H	1.948423	-1.194719	2.130324
H	4.208801	0.848870	2.479508
H	2.555268	0.907619	3.094289
C	3.898397	1.618440	0.144893
C	3.546268	1.623833	-1.362413
H	4.660811	0.853804	0.308660
H	4.322485	2.580965	0.459202
H	3.887785	0.690088	-1.817751
H	-4.153226	-0.777676	2.066066
H	-4.967499	-2.213826	1.428090
H	-5.490286	-0.965440	-0.511261
H	-4.640940	0.409383	0.209652
H	4.054749	2.454112	-1.874688
H	-4.512814	0.873589	-2.026652

Table S4 Cartesian coordinates of $[Cu^{III}_2(\mathbf{Lb})_2(O^{2-})_2]^{2+}$ (**2b**) in the closed-shell singlet state.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.865905	-2.480584	1.764365
C	1.757509	-3.623312	0.744270
H	2.514781	-2.800464	2.592445
C	1.117147	-3.255577	-0.600964
H	2.747544	-4.060502	0.571743
H	1.149366	-4.416977	1.194657
N	1.680963	-2.001254	-1.209743
H	1.274992	-4.083353	-1.307647
H	0.037490	-3.098145	-0.501796
C	3.169631	-1.939722	-1.129705
C	1.205120	-1.868680	-2.606808
N	2.435963	-1.225726	1.161383
H	0.886465	-2.212565	2.177410
H	1.533575	-0.908234	-3.011311
H	1.605116	-2.688519	-3.219977
H	0.112229	-1.891897	-2.605653
C	3.620830	-1.539990	0.293548
C	2.763328	1.239162	1.860009
C	3.250613	1.651291	0.487941
Cu	0.982186	-0.599257	-0.011701
O	-0.465616	-0.218419	-1.015752
O	0.014193	0.251982	1.283538
Cu	-1.363503	0.750647	0.233292
N	-2.691234	1.480319	-1.029807
C	-1.902543	2.609272	-1.639793
C	-1.014039	3.330571	-0.601090

C	-1.590117	3.473948	0.821341
N	-2.069640	2.164318	1.411228
C	-1.669077	2.025006	2.829742
C	-3.540070	1.992288	1.244354
C	-3.089018	0.493746	-2.082062
H	-2.054405	2.869463	3.417710
H	-0.577857	1.986497	2.883092
H	-2.419674	4.191894	0.855548
H	-0.795425	3.852415	1.470194
H	-0.793801	4.338079	-0.975686
H	-0.049841	2.807732	-0.531887
H	-2.603198	3.299393	-2.127660
H	-1.254972	2.173746	-2.405979
N	2.509670	1.226783	-0.563683
C	2.834948	1.646118	-1.797110
C	3.918712	2.493713	-2.062652
C	4.704960	2.915649	-0.980276
C	4.362959	2.490760	0.312039
H	4.943101	2.809106	1.176733
H	5.563401	3.567861	-1.138146
H	4.134277	2.805618	-3.082755
H	2.195848	1.294235	-2.608165
H	-3.663894	1.035064	-2.848486
C	-3.858280	2.033274	-0.250225
H	-2.070919	1.086859	3.223237
H	-2.155018	0.135860	-2.528287
C	-3.923901	-0.709653	-1.606526
H	-4.204271	-1.252835	-2.516750
H	-4.867576	-0.369054	-1.159355
C	-2.156046	-3.398809	1.217450
C	-2.608114	-3.918523	-0.004911
C	-3.164154	-3.042472	-0.947260
C	-3.264924	-1.674037	-0.640756

N	-2.820747	-1.177225	0.534240
C	-2.275140	-2.020154	1.429236
H	-1.713038	-4.034952	1.981704
H	-2.523251	-4.982963	-0.221994
H	-3.521414	-3.412139	-1.907073
H	-1.892073	-1.560054	2.340056
H	-4.051195	3.055033	-0.592671
H	-4.755568	1.446946	-0.449004
H	-4.085907	2.771899	1.794364
H	3.495464	-1.175828	-1.839742
H	3.597445	-2.901216	-1.442576
H	4.241505	-0.645743	0.235385
H	4.216445	-2.322435	0.779014
C	2.815646	-0.259723	2.241851
H	3.816931	-0.544301	2.593865
H	2.114462	-0.407022	3.068692
H	3.322804	1.782232	2.629848
H	1.710777	1.537458	1.913711
H	-3.797273	1.011137	1.653404