Supporting Information
for

Valence-to-Core X-ray Emission Spectroscopy as a Probe of O-O Bond Activation in Cu_2O_2 complexes

George E. Cutsail III,[a] Nicole L. Gagnon,[b] Andrew D. Spaeth,[b] William B. Tolman[b,c] and Serena DeBeer*[a]

[a] Dr. G. E. Cutsail III, Prof. Dr. Serena DeBeer
Inorganic Spectroscopy
Max Planck Institute for Chemical Energy Conversion
Stiftstraße 34-36
D-45470 Mülheim an der Ruhr, Germany
E-mail: serena.debeer@cec.mpg.de

[b] Dr. N. L. Gagnon, Dr. A. D. Spaeth, Prof. Dr. W. B. Tolman
Department of Chemistry, Center for Metals in Biocatalysis
University of Minnesota
207 Pleasant St. SE
Minneapolis, Minnesota 55455, United States

[c] Prof. Dr. W. B. Tolman (Present Address)
Department of Chemistry
One Brookings Hall
Washington University in St. Louis
St. Louis, MO, USA

Experimental

All X-ray absorption and emission data were collected at beam line ID26 at the European Synchrotron Research Facility (ESRF) (6 GeV, 200 mA). All samples were kept at 20 K in a liquid helium cryostat. A Si(311) double crystal monochromator was employed with the incident energy calibrated to the first inflection point of a Cu foil at 8980.3 eV. Cu Kβ high-energy fluorescence detected (HERFD) XAS was detected with a 1 m radius Johann spectrometer[1] equipped with five Si(553) analyzer crystals and a Ketek silicon-drift energy detector in a Rowland geometry at the maximum of the Kβ emission. The spectrometer was calibrated by scanning of the elastic lines in the Cu Kβ emission range. This resulted in an observed Kβ emission maximum for anhydrous CuCl (Strem Chemicals) at 8903.6 eV (**Figure S4**). All XES spectra were collected non-resonantly with an incident energy of 9.5 keV.

Assessment of short (5 to 60 sec) XAS scans employing a fast scanning monochromator were used to maximize exposure times and assess radiation damage processes and dwell time limits. When necessary, the incident beam was attenuated by insertion of various numbers of aluminum foils into the beam path. Only scans that showed no evidence of radiation damage were included in the final analysis. The beam exposure limit per spot, as determined by this procedure, limited both the exposure times of XAS and XES measurements.

To increase efficiency of XES data collection, including increasing S/N and decreasing the overall deadtime of data collection because of motor movements (e.g. settling time), the VtC XES spectrum was collected in smaller segments on fresh spots to allow for increased dwell times. A small amount of energy overlap with the neighboring segments was collected for splining of complete spectrum over the VtC region. However, the simultaneous collection of TFY recorded by a diode detector directly above spectrometer's analyzer crystals is a good reporter of the sample's concentration at that sample spot and was utilized for normalization. All data were processed within Matlab 2017a. The integrated intensity of the Cu Kβ mainline fit was normalize to a unit of 1 and used for the scaling of the VtC spectra.

DFT calculations were performed with the ORCA[2] electronic structure package (v 4.0) employing the BP86 functionals[3 5648] with the def2 variants of the all-electron Gaussian basis sets of split-valence (def2-SVP) and triple-valence (def2-TZVP) quality as developed by the Aldrichs group.[4] Calculation employed the resolution of identity approximation for the computation of the Coulomb terms.[5] Only the singlet spin multiplicity was calculated for all complexes as broken symmetry has been explored previously and shown not to be more stable.[6] VtC XES were calculated by a one electron method and corrected for spin-orbit coupling using spin-orbit mean-field methods.[7]

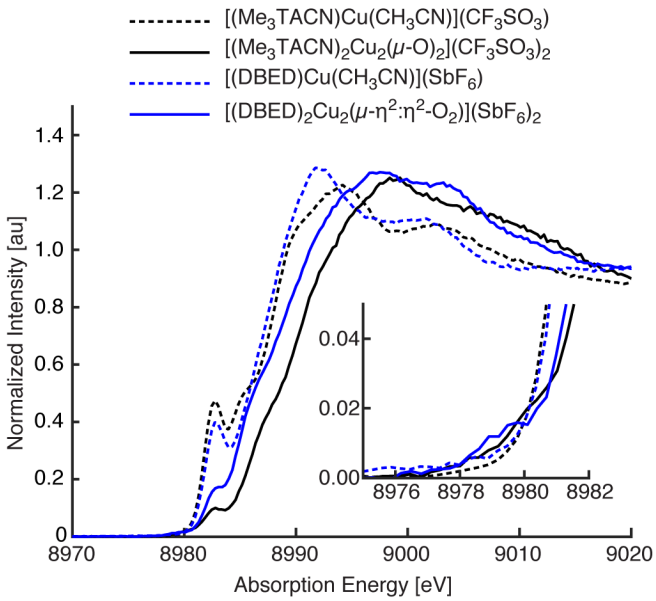

Figure S1. Kβ HERFD of $[(Me_3TACN)Cu^{I}(CH_3CN)](CF_3SO_3)$, $[(Me_3TACN)_2Cu^{III}_2(\mu\text{-}O)_2](CF_3SO_3)_2$, $[(DBED)Cu^{I}(CH_3CN)](SbF_6)$ and $[(DBED)_2Cu^{II}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)](SbF_6)_2$

The X-ray absorption edges of the Cu(I) precursor complexes exhibit the lowest energy features at 8982.7 eV, consistent with a the dipole allowed 1s to 4p transition of Cu(I) centers. The rising-edge of each precursor is low in energy, confirming the Cu(I) oxidation state. The closed-shell, d^{10}, $[(Me_3TACN)Cu^{I}(CH_3CN)]^+$ and $[(DBED)Cu^{I}(CH_3CN)]^+$ complexes exhibit no 1s to 3d pre-edge transitions, as expected.

Upon reaction with O_2, the absorption edges of the reaction products, $[(Me_3TACN)_2Cu_2(\mu\text{-}O)_2]^{2+}$ and $[(DBED)_2Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]^{2+}$, exhibit edges shifted to higher energy than their precursors**,** $[(Me_3TACN)Cu^{I}(CH_3CN)]^+$ and $[(DBED)Cu^{I}(CH_3CN$, respectively. It is immediately observed that the edge of $[(Me_3TACN)_2Cu_2(\mu\text{-}O)_2]^{2+}$ is at the highest energy, forming an energy trend of $[(Me_3TACN)Cu^{I}(CH_3CN)]^+ \approx [(DBED)Cu^{I}(CH_3CN)]^+ < [(DBED)_2Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]^{2+}$, $< [(Me_3TACN)_2Cu_2(\mu\text{-}O)_2]^{2+}$. Upon close inspection, a small pre-edge feature in both $[(Me_3TACN)_2Cu_2(\mu\text{-}O)_2]^{2+}$ at ~8980 eV and $[(DBED)_2Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]^{2+}$, at ~8979 eV are visible as low-energy shoulders at the onset of the rising edge, consistent with previous studies.[8] While K-edge 1s to 3d pre-edge transitions are dipole-forbidden and inherently weak, it is surprising that these pre-edges are not more pronounced in the HERFD-XAS, despite the improved baseline. These pre-edge transition for $[(DBED)_2Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]^{2+}$, are slightly higher in energy than pre-edges typically observed for Cu(II) centers at ~8978 eV.[8]

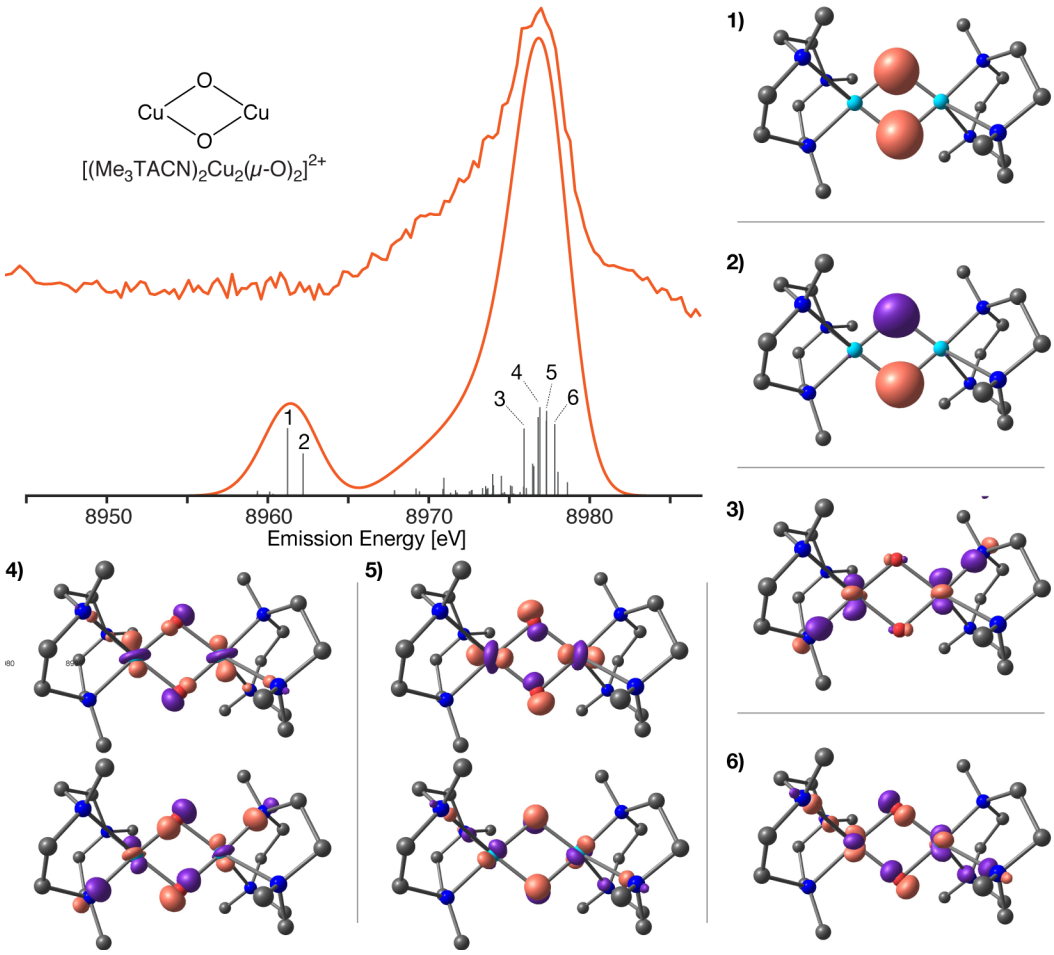

Figure S2. MO plots of additional selected VtC transitions of $[(Me_3TACN)_2Cu_2(\mu\text{-}O)_2]^{2+}$. MOs 1 and 2 exhibit the oxygen 2s(α),2s(α) and 2s(α),2s(β) orbitals. Transitions in 4 shows the same multiple spin configuration of the O 2p orbitals.

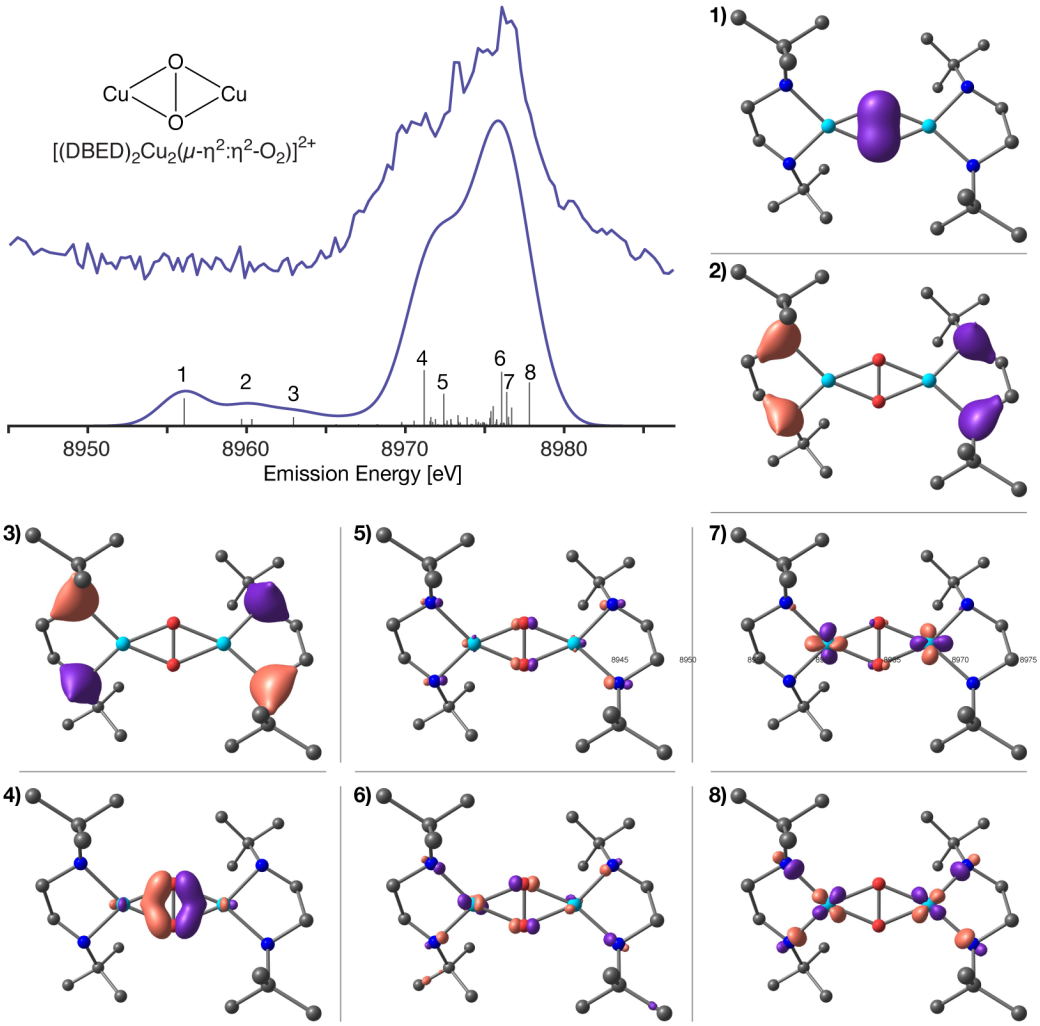

Figure S3. MO plots of additional selected VtC transitions of $[(DBED)_2Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]^{2+}$. MOs 2 and 3 exhibit the nitrogen 2s(α),2s(α) and 2s(α),2s(β) orbitals. Diffuse ligand N and O 2p character is observed in higher energy transitions (6 – 8).

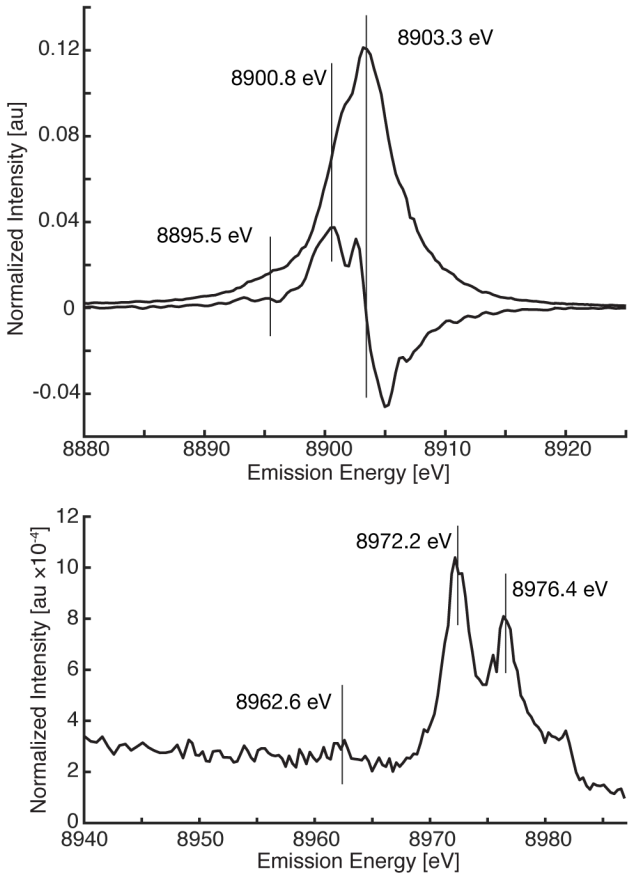

Figure S4. Calibrated Cu Kβ mainline (top) and VtC emission of anhydrous CuCl collected with an incident energy of 9.5 keV.

Optimized Coordinates for $[(DBED)_2Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]^{2+}$

Cu	1.792896	0.000000	0.734090
Cu	-1.793089	-0.009039	0.732720
O	0.000000	0.000000	1.484962
O	0.000000	0.000000	0.000000
N	3.225159	-0.270333	-0.687684
H	3.279155	0.614522	-1.212317
N	3.264264	0.287817	2.104909
H	3.404915	-0.623821	2.564780
N	-3.268389	-0.315977	2.096711
H	-3.436253	0.600555	2.536682
N	-3.222837	0.241146	-0.696576
H	-3.241031	-0.641853	-1.226676
C	4.495137	-0.403888	0.091692
H	5.381578	-0.205810	-0.543108
H	4.570827	-1.450147	0.448215
C	2.962608	-1.369260	-1.731163
C	4.248948	-1.663466	-2.528290
H	5.031009	-2.149120	-1.913628
H	4.672526	-0.744876	-2.983234
H	4.013999	-2.359173	-3.357168
C	2.466423	-2.623711	-0.997174
H	3.221745	-3.030452	-0.295077
H	2.245011	-3.425767	-1.728143
H	1.529902	-2.415906	-0.436950
C	1.880849	-0.818997	-2.670918
H	1.631949	-1.571716	-3.442974
H	2.224923	0.094379	-3.199107
H	0.949918	-0.580675	-2.120923
C	4.475263	0.556201	1.271502
H	5.406844	0.445002	1.862050
H	4.427264	1.606430	0.921779
C	2.987796	1.292707	3.234833
C	4.286535	1.594557	4.008967
H	4.048043	2.215745	4.894295
H	5.022160	2.162868	3.407824
H	4.767759	0.667339	4.383255
C	2.400169	2.570453	2.617236
H	1.454156	2.355757	2.076341
H	3.106099	3.067516	1.922294
H	2.168338	3.302619	3.414851
C	1.974748	0.612951	4.167611
H	1.041252	0.353611	3.630690
H	1.710727	1.292294	5.000126
H	2.394923	-0.311176	4.617579
C	-4.461819	-0.628899	1.252537
H	-5.402450	-0.547075	1.833318
H	-4.374238	-1.678119	0.906348
C	-2.983649	-1.289856	3.249923
C	-1.977955	-0.579005	4.166334
H	-1.722896	-1.227185	5.026545

H	-2.399634	0.361032	4.580968
H	-1.039287	-0.340368	3.628404
C	-2.383844	-2.578535	2.667698
H	-3.087833	-3.108740	1.994949
H	-2.139371	-3.282672	3.486637
H	-1.443548	-2.368838	2.115078
C	-4.280635	-1.585221	4.029011
H	-5.011395	-2.174409	3.441485
H	-4.773049	-0.655482	4.382972
H	-4.035426	-2.183714	4.928137
C	-4.503877	0.327832	0.070262
H	-5.376329	0.097202	-0.573035
H	-4.621299	1.370350	0.425922
C	-2.990303	1.355579	-1.730170
C	-1.844402	0.878935	-2.633779
H	-0.912308	0.722773	-2.057010
H	-1.637339	1.640814	-3.409637
H	-2.102764	-0.064900	-3.157754
C	-2.598871	2.637083	-0.980281
H	-3.409699	3.010910	-0.324340
H	-2.374804	3.444154	-1.704674
H	-1.686691	2.480497	-0.365477
C	-4.262590	1.571497	-2.573970
H	-4.600911	0.632482	-3.058086
H	-4.044418	2.295981	-3.383086
H	-5.102757	1.991107	-1.987580

Optimized Coordinates for $[(Me_3TACN)_2Cu_2(\mu\text{-}O)_2]^{2+}$

Cu	8.154655	1.013951	4.161386
O	9.010997	1.616181	5.698949
N	8.283084	-0.731863	2.777376
N	9.284690	1.977351	2.815500
N	6.465231	1.531228	2.822065
C	8.360377	3.031980	2.267877
H	8.868828	3.595237	1.453780
H	8.171977	3.744986	3.094704
C	8.253592	-2.009659	3.516451
C	9.736561	0.999619	1.748477
H	10.781440	1.229014	1.459298
H	9.124429	1.162036	0.843671
C	7.046967	2.425252	1.777059
H	7.202841	1.848111	0.846032
H	6.340542	3.239700	1.511205
C	10.458415	2.619259	3.468284
C	9.629547	-0.447035	2.216542
H	9.881963	-1.132430	1.373334
H	10.365872	-0.643595	3.021718
C	5.417250	2.207559	3.615078
C	6.009581	0.217576	2.316909
H	5.245097	0.329738	1.514355
H	5.521627	-0.294665	3.169458
C	7.174279	-0.636102	1.791579
H	6.790026	-1.647078	1.542953
H	7.558407	-0.225775	0.838791
O	7.151295	0.218604	5.446070
Cu	8.008593	0.819699	6.983608
N	7.893922	2.560391	8.372313
N	6.877503	-0.142378	8.329521
N	9.699949	0.287895	8.317650
C	7.797391	-1.203727	8.871450
H	7.287841	-1.766822	9.684971
H	7.979764	-1.915054	8.041815
C	7.928700	3.839883	7.636272
C	6.433557	0.834556	9.400627
H	5.388185	0.609958	9.691814
H	7.047099	0.666337	10.303435
C	9.115491	-0.606061	9.361016
H	8.965111	-0.031325	10.294434
H	9.817700	-1.425533	9.622661
C	5.698570	-0.775919	7.677769
C	6.547184	2.281720	8.935956
H	6.300978	2.966677	9.781298
H	5.810034	2.484180	8.133017
C	10.742168	-0.391763	7.520110
C	10.163762	1.597490	8.825420
H	10.929103	1.479317	9.626319
H	10.653028	2.109365	7.973390
C	9.004735	2.456093	9.355262

H	9.394778	3.464461	9.605406
H	8.620576	2.045517	10.307891
H	11.004859	3.248912	2.734124
H	11.134626	1.838797	3.859893
H	10.115854	3.240402	4.314781
H	5.151471	-1.405996	8.411066
H	6.035512	-1.395078	6.827533
H	5.024781	0.009516	7.291921
H	7.160886	3.833233	6.840453
H	8.915022	3.959290	7.152299
H	7.744803	4.702669	8.314596
H	9.018914	-1.996503	4.314609
H	8.444651	-2.873179	2.841007
H	7.266495	-2.133846	3.997646
H	10.352015	-1.353128	7.136766
H	11.009854	0.245341	6.656849
H	11.650220	-0.595453	8.129216
H	5.800933	3.172425	3.996097
H	4.509606	2.403669	3.002945
H	5.151359	1.571713	4.479805

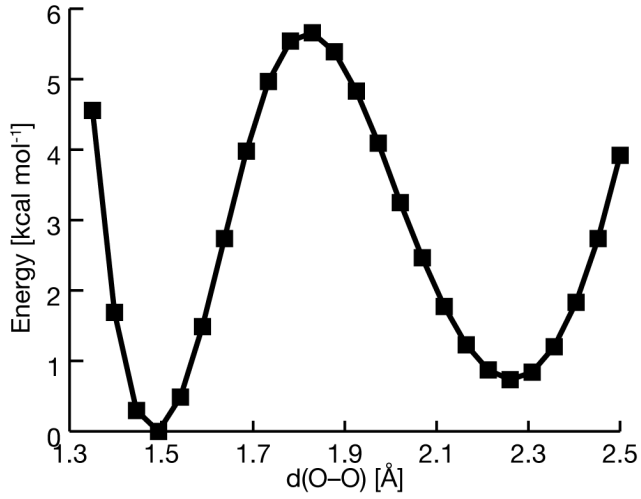

Figure S5. Relaxed Surface Scan of O-O bond length with DBED ligands

Coordinates for $[(DBED)_2Cu_2(O_2)]^{2+}$; d(O–O) = 1.485 Å

Cu	2.495559	8.570828	2.000783
Cu	4.276521	5.474200	2.315078
O	2.843484	6.671964	1.773801
O	3.919355	7.366299	2.525802
N	2.683209	10.420388	2.831223
H	3.458858	10.880636	2.333558
N	0.908695	9.254946	0.932676
H	0.070220	8.987718	1.469244
N	3.876183	3.504615	2.012895
H	4.078842	3.328588	1.018039
N	6.142361	4.955877	2.947110
H	6.113537	5.020060	3.974766
C	1.423271	11.126753	2.442035
H	1.536446	12.226448	2.518526
H	0.627555	10.825997	3.151885
C	3.044691	10.472505	4.325218
C	2.841423	11.899598	4.871746
H	1.775297	12.194933	4.909705
H	3.398938	12.652770	4.278360
H	3.226100	11.951856	5.908828
C	2.160988	9.462241	5.071542
H	1.082519	9.708556	4.999967
H	2.417515	9.460253	6.148957
H	2.320450	8.431403	4.689385
C	4.526210	10.082810	4.422026
H	4.849810	10.085748	5.480267
H	5.173708	10.800498	3.876776
H	4.704763	9.067350	4.018421
C	1.037856	10.740998	1.021721
H	0.093766	11.247933	0.737722

H	1.816952	11.063097	0.302795
C	0.708287	8.679399	-0.478600
C	-0.354102	9.496202	-1.241035
H	-0.579790	8.994745	-2.202374
H	-0.013214	10.520438	-1.486441
H	-1.307464	9.560104	-0.676753
C	2.058329	8.704215	-1.210805
H	2.817877	8.099546	-0.671301
H	2.447729	9.733162	-1.344915
H	1.946251	8.270630	-2.223443
C	0.212094	7.239433	-0.282152
H	0.941192	6.635221	0.292569
H	0.065421	6.751590	-1.264390
H	-0.764370	7.215856	0.246048
C	4.931862	2.809460	2.811084
H	5.018169	1.741542	2.526675
H	4.637959	2.846968	3.879078
C	2.434356	3.025619	2.238994
C	1.609971	3.600797	1.078757
H	0.550592	3.295342	1.176547
H	1.968684	3.222221	0.098240
H	1.646376	4.708024	1.066951
C	1.941811	3.569953	3.588255
H	2.526035	3.175936	4.444263
H	0.890985	3.263544	3.755927
H	1.973882	4.679934	3.608417
C	2.374578	1.485550	2.207840
H	2.882076	1.017099	3.073484
H	2.807362	1.072153	1.272976
H	1.315647	1.162892	2.244199
C	6.265779	3.507995	2.593424
H	7.055511	3.011587	3.191833
H	6.564378	3.438878	1.528912
C	7.307330	5.852074	2.495316
C	7.164201	7.172724	3.264773
H	6.208066	7.678017	3.027419
H	7.986735	7.859379	2.986867
H	7.221996	7.014609	4.361954
C	7.181167	6.083546	0.982600
H	7.287307	5.147962	0.398760
H	7.980027	6.768729	0.638121
H	6.207566	6.554354	0.727629
C	8.654556	5.189227	2.845961
H	8.725280	4.944159	3.925554
H	9.477877	5.893896	2.616338
H	8.848179	4.269999	2.260022

Coordinates for $[(DBED)_2Cu_2(O_2)]^{2+}$; d(O–O) = 1.60 Å

Cu	2.514367	8.533232	2.007107
Cu	4.254832	5.510320	2.312076
O	2.797760	6.643187	1.750957

O	3.961251	7.392221	2.554224
N	2.683838	10.378458	2.850936
H	3.465559	10.841112	2.364958
N	0.943036	9.229586	0.921539
H	0.097995	8.954557	1.443967
N	3.854265	3.536860	2.035450
H	4.045984	3.354051	1.039547
N	6.127449	4.991299	2.923522
H	6.109674	5.069303	3.950576
C	1.428982	11.088403	2.452819
H	1.540743	12.187168	2.542674
H	0.623697	10.779937	3.148518
C	3.028450	10.421212	4.349439
C	2.822201	11.846094	4.901057
H	1.756374	12.143481	4.929464
H	3.387600	12.601088	4.317480
H	3.196124	11.891891	5.942371
C	2.134467	9.408978	5.080765
H	1.057439	9.658436	4.999646
H	2.380120	9.400932	6.160680
H	2.295241	8.380111	4.694564
C	4.508021	10.028168	4.461118
H	4.820678	10.028188	5.522668
H	5.162913	10.744740	3.923283
H	4.687729	9.012433	4.057704
C	1.065818	10.715105	1.023911
H	0.125005	11.221251	0.728280
H	1.855712	11.045122	0.320381
C	0.763177	8.667979	-0.498429
C	-0.294675	9.487733	-1.264481
H	-0.507802	8.994087	-2.232716
H	0.044540	10.515594	-1.496754
H	-1.254444	9.542228	-0.710102
C	2.121318	8.708137	-1.215085
H	2.878144	8.101437	-0.674481
H	2.506813	9.740491	-1.333334
H	2.021780	8.285870	-2.233711
C	0.272411	7.223617	-0.324117
H	0.999122	6.618115	0.252869
H	0.141173	6.745053	-1.313123
H	-0.709833	7.188464	0.192561
C	4.917022	2.845170	2.827271
H	4.996110	1.774619	2.550938
H	4.636015	2.892605	3.898289
C	2.414579	3.058684	2.280552
C	1.578159	3.623350	1.124043
H	0.519177	3.321422	1.236350
H	1.925683	3.235836	0.142977
H	1.616376	4.730747	1.102253
C	1.935286	3.613491	3.630296
H	2.528661	3.227112	4.483488
H	0.886862	3.306258	3.810798

H	1.965682	4.723386	3.640505
C	2.355316	1.518284	2.262248
H	2.871269	1.056549	3.126469
H	2.778097	1.097324	1.326206
H	1.296697	1.196287	2.312126
C	6.248584	3.539309	2.586821
H	7.045511	3.051354	3.182478
H	6.535435	3.457404	1.520065
C	7.287581	5.881584	2.446365
C	7.160231	7.208467	3.207456
H	6.200287	7.713749	2.983186
H	7.978354	7.892179	2.909730
H	7.237087	7.058757	4.304676
C	7.139543	6.099839	0.933586
H	7.228927	5.157291	0.358386
H	7.939292	6.773996	0.569967
H	6.166417	6.576431	0.688821
C	8.638846	5.218532	2.781737
H	8.725787	4.980169	3.861679
H	9.459246	5.920978	2.535543
H	8.822456	4.295683	2.198352

Coordinates for $[(DBED)_2Cu_2(O_2)]^{2+}$; d(O–O) = 1.70 Å

Cu	2.537951	8.487391	2.008041
Cu	4.229461	5.553352	2.308012
O	2.763535	6.618669	1.720345
O	3.996554	7.415572	2.577438
N	2.686745	10.327500	2.869951
H	3.474738	10.794507	2.398315
N	0.981516	9.198835	0.907314
H	0.130118	8.913393	1.413837
N	3.828729	3.574380	2.058703
H	4.005620	3.382491	1.061711
N	6.109620	5.032048	2.899076
H	6.104937	5.123551	3.925225
C	1.436985	11.041433	2.464393
H	1.546842	12.139066	2.568807
H	0.622939	10.724372	3.145987
C	3.012352	10.357187	4.373666
C	2.797944	11.777290	4.934448
H	1.731591	12.073467	4.953907
H	3.369046	12.537696	4.363509
H	3.160680	11.814542	5.980076
C	2.110289	9.338034	5.085221
H	1.034052	9.586760	4.992197
H	2.341974	9.322512	6.168141
H	2.277605	8.312591	4.693366
C	4.490927	9.965082	4.500364
H	4.790856	9.956125	5.565593
H	5.151462	10.686383	3.975862
H	4.675990	8.952441	4.090317

C	1.095509	10.683504	1.026962
H	0.156892	11.188413	0.722647
H	1.894299	11.024372	0.338658
C	0.824558	8.655422	-0.522947
C	-0.229992	9.477818	-1.290646
H	-0.428876	8.994160	-2.266949
H	0.104966	10.510596	-1.506932
H	-1.196429	9.519349	-0.746745
C	2.190980	8.716038	-1.222416
H	2.946161	8.107576	-0.681817
H	2.570215	9.752653	-1.322180
H	2.105572	8.307422	-2.247762
C	0.343824	7.205039	-0.375224
H	1.070332	6.599372	0.202598
H	0.230190	6.738334	-1.372130
H	-0.644025	7.153675	0.129238
C	4.899634	2.886676	2.842574
H	4.972252	1.813502	2.574790
H	4.632530	2.944539	3.916593
C	2.391357	3.100541	2.330060
C	1.538922	3.656164	1.181198
H	0.480274	3.360883	1.313302
H	1.869496	3.258398	0.198379
H	1.582045	4.763668	1.149357
C	1.933410	3.669153	3.681466
H	2.537813	3.289193	4.529736
H	0.887009	3.366093	3.879711
H	1.966349	4.778863	3.680126
C	2.329502	1.560266	2.326778
H	2.856764	1.105124	3.187633
H	2.737664	1.130096	1.388476
H	1.271009	1.240999	2.394805
C	6.228223	3.576440	2.578429
H	7.032396	3.096258	3.170560
H	6.503246	3.482500	1.509635
C	7.264438	5.915581	2.394549
C	7.153564	7.248913	3.146565
H	6.188801	7.752739	2.936898
H	7.965532	7.930164	2.826883
H	7.251900	7.108113	4.243282
C	7.092378	6.120402	0.882374
H	7.164843	5.171334	0.315738
H	7.891672	6.783984	0.498880
H	6.119397	6.602417	0.648998
C	8.619430	5.251829	2.713171
H	8.723449	5.020332	3.793122
H	9.436611	5.951739	2.449656
H	8.792475	4.325260	2.132533

Coordinates for $[(DBED)_2Cu_2(O_2)]^{2+}$; d(O–O) = 1.80 Å

Cu	2.563957	8.427711	2.008472

Cu	4.199174	5.605442	2.304399
O	2.731602	6.590790	1.688267
O	4.027835	7.438207	2.605690
N	2.680568	10.258235	2.898562
H	3.470981	10.736775	2.442480
N	1.029791	9.154170	0.883816
H	0.169407	8.846221	1.361349
N	3.792013	3.621071	2.092997
H	3.947338	3.412558	1.095683
N	6.087864	5.082319	2.867255
H	6.104219	5.193228	3.891424
C	1.430397	10.967185	2.488121
H	1.528061	12.063307	2.617311
H	0.608030	10.626859	3.148282
C	2.987842	10.273364	4.407665
C	2.752779	11.685254	4.980181
H	1.683597	11.971381	4.992958
H	3.322412	12.457294	4.423450
H	3.105562	11.714297	6.029531
C	2.087108	9.237959	5.096803
H	1.009540	9.475550	4.990163
H	2.303116	9.216109	6.182856
H	2.271715	8.218211	4.698856
C	4.469033	9.895456	4.547370
H	4.756674	9.877095	5.615952
H	5.127594	10.630087	4.038903
H	4.668736	8.889655	4.126442
C	1.121302	10.637235	1.038838
H	0.181464	11.134763	0.726671
H	1.929563	11.004073	0.375248
C	0.914609	8.647019	-0.564891
C	-0.143432	9.468017	-1.328656
H	-0.315478	9.005357	-2.320183
H	0.173043	10.512885	-1.512784
H	-1.119978	9.475637	-0.801239
C	2.292247	8.758440	-1.235204
H	3.053203	8.157566	-0.694444
H	2.647306	9.805864	-1.306146
H	2.235153	8.370744	-2.270385
C	0.466479	7.182387	-0.469263
H	1.202129	6.577936	0.098717
H	0.377529	6.744776	-1.481987
H	-0.526312	7.090794	0.019651
C	4.874483	2.940852	2.867133
H	4.937315	1.863832	2.612593
H	4.627396	3.016038	3.944822
C	2.357585	3.157167	2.404264
C	1.483018	3.692013	1.262254
H	0.425811	3.406205	1.424359
H	1.789747	3.271140	0.281329
H	1.531831	4.798877	1.206528
C	1.931135	3.756303	3.752635

H	2.553726	3.394305	4.595553
H	0.889089	3.459641	3.980947
H	1.965491	4.865371	3.724878
C	2.292911	1.617639	2.433702
H	2.834605	1.178106	3.293670
H	2.682374	1.167939	1.496669
H	1.235003	1.302696	2.527467
C	6.198474	3.621548	2.568780
H	7.011533	3.150376	3.155903
H	6.455829	3.510059	1.497398
C	7.235913	5.953144	2.321568
C	7.156726	7.293724	3.064394
H	6.186369	7.799076	2.883988
H	7.960024	7.968697	2.710909
H	7.293556	7.161304	4.158157
C	7.023584	6.143754	0.812624
H	7.060742	5.186182	0.257075
H	7.824928	6.785700	0.397941
H	6.054391	6.642745	0.601560
C	8.593372	5.280498	2.609103
H	8.724036	5.053832	3.687185
H	9.407792	5.974153	2.321491
H	8.745061	4.350375	2.028375

Coordinates for $[(DBED)_2Cu_2(O_2)]^{2+}$; d(O–O) = 1.90 Å

Cu	2.590122	8.375761	2.014345
Cu	4.168455	5.653647	2.303119
O	2.695762	6.566013	1.664733
O	4.061649	7.460928	2.636061
N	2.675758	10.199355	2.917473
H	3.458033	10.691562	2.461458
N	1.066822	9.101364	0.874728
H	0.205088	8.764934	1.330051
N	3.757491	3.668712	2.112973
H	3.899655	3.453365	1.115015
N	6.060196	5.127628	2.844433
H	6.088231	5.250760	3.867067
C	1.413252	10.890516	2.515303
H	1.487606	11.985272	2.668323
H	0.595029	10.518353	3.163206
C	2.985112	10.215578	4.428068
C	2.723624	11.621617	5.003318
H	1.649377	11.887695	5.022595
H	3.276626	12.405912	4.446954
H	3.080969	11.654179	6.051068
C	2.104441	9.162348	5.115862
H	1.022425	9.379222	5.009273
H	2.320733	9.145059	6.201929
H	2.309232	8.146962	4.717784
C	4.473744	9.867615	4.565238
H	4.762070	9.851462	5.633721

H	5.116429	10.617670	4.058810
H	4.691673	8.867839	4.139203
C	1.123116	10.583331	1.058681
H	0.174841	11.063849	0.746232
H	1.928341	10.980700	0.409209
C	0.988225	8.624992	-0.589236
C	-0.058896	9.456172	-1.356919
H	-0.205963	9.011824	-2.360801
H	0.253316	10.506746	-1.513701
H	-1.046852	9.445738	-0.851156
C	2.379472	8.763669	-1.224848
H	3.133012	8.155397	-0.682432
H	2.727317	9.815285	-1.263249
H	2.347841	8.401319	-2.270252
C	0.549227	7.155785	-0.539082
H	1.277753	6.543902	0.030028
H	0.485123	6.743369	-1.564377
H	-0.453612	7.045077	-0.075140
C	4.846229	2.990188	2.879460
H	4.900531	1.911030	2.632571
H	4.612772	3.075529	3.959413
C	2.325012	3.207221	2.447642
C	1.438092	3.714774	1.302895
H	0.382549	3.434553	1.484702
H	1.733371	3.269213	0.329419
H	1.488932	4.819986	1.220207
C	1.911611	3.832292	3.788095
H	2.549697	3.494660	4.629588
H	0.875988	3.530198	4.037421
H	1.934812	4.940356	3.735063
C	2.266535	1.668439	2.508952
H	2.813014	1.247422	3.375122
H	2.651925	1.201265	1.578842
H	1.209765	1.353121	2.614021
C	6.166462	3.664158	2.558500
H	6.986682	3.199049	3.140153
H	6.410743	3.543417	1.485100
C	7.207508	5.988175	2.274556
C	7.163506	7.326622	3.023939
H	6.192504	7.840178	2.873387
H	7.963122	7.994483	2.649107
H	7.331887	7.187969	4.112638
C	6.963061	6.185006	0.771318
H	6.960546	5.226479	0.215895
H	7.772084	6.804155	0.337288
H	6.003925	6.711693	0.584811
C	8.562230	5.296668	2.529077
H	8.713267	5.060892	3.602465
H	9.377377	5.984695	2.230154
H	8.692020	4.370203	1.937561

Coordinates for $[(DBED)_2Cu_2(O_2)]^{2+}$; d(O–O) = 2.10 Å

Cu	2.631370	8.291809	2.022576
Cu	4.111299	5.720507	2.301951
O	2.619378	6.515362	1.622050
O	4.128364	7.500113	2.700580
N	2.640952	10.109596	2.932546
H	3.384832	10.641080	2.456199
N	1.125046	8.983458	0.841962
H	0.271215	8.563467	1.237937
N	3.659684	3.744329	2.115931
H	3.710326	3.556795	1.103494
N	6.008017	5.158576	2.769267
H	6.054322	5.220130	3.797163
C	1.331336	10.723475	2.557275
H	1.329031	11.813455	2.755156
H	0.543033	10.267301	3.187900
C	2.979231	10.157505	4.439174
C	2.641394	11.551496	5.005883
H	1.553393	11.749401	5.056377
H	3.128811	12.363842	4.428856
H	3.026567	11.616447	6.042247
C	2.177503	9.061609	5.155194
H	1.082125	9.208193	5.063294
H	2.411559	9.076927	6.237602
H	2.441518	8.056436	4.768844
C	4.489327	9.909824	4.551360
H	4.794775	9.918833	5.615167
H	5.071463	10.699297	4.031510
H	4.762302	8.924983	4.124601
C	1.068812	10.456113	1.090272
H	0.088621	10.875374	0.789379
H	1.843249	10.939662	0.463073
C	1.153575	8.576846	-0.650228
C	0.152787	9.437845	-1.446982
H	0.089126	9.040680	-2.479024
H	0.457028	10.499035	-1.530565
H	-0.869457	9.387619	-1.017842
C	2.584877	8.761921	-1.174305
H	3.300214	8.118346	-0.621718
H	2.927055	9.815011	-1.115527
H	2.631982	8.473504	-2.242475
C	0.725105	7.104591	-0.712986
H	1.416234	6.463961	-0.130117
H	0.732694	6.755879	-1.763876
H	-0.307744	6.963973	-0.329537
C	4.797300	3.028026	2.768354
H	4.826137	1.962280	2.466500
H	4.642643	3.060474	3.864885
C	2.253031	3.290031	2.570217
C	1.274851	3.759745	1.484902
H	0.240641	3.473074	1.757263
H	1.498695	3.289867	0.503858

H	1.309071	4.862359	1.371061
C	1.945497	3.949120	3.922433
H	2.669415	3.658308	4.710299
H	0.946539	3.627240	4.275398
H	1.932408	5.054748	3.833157
C	2.209120	1.752872	2.678370
H	2.815131	1.357820	3.516448
H	2.530520	1.260906	1.737083
H	1.163089	1.439408	2.864548
C	6.091804	3.715975	2.389823
H	6.950367	3.220467	2.883928
H	6.258263	3.658557	1.296042
C	7.158078	6.040110	2.229647
C	7.183400	7.304220	3.099327
H	6.218039	7.843560	3.039072
H	7.982459	7.986062	2.749546
H	7.397840	7.060702	4.161437
C	6.861527	6.376912	0.761147
H	6.776306	5.470859	0.128144
H	7.688462	6.982803	0.341946
H	5.929848	6.972012	0.668387
C	8.500996	5.294010	2.366164
H	8.687632	4.960605	3.407448
H	9.319361	5.991597	2.100238
H	8.588824	4.423244	1.687722

Coordinates for $[(DBED)_2Cu_2(O_2)]^{2+}$; d(O–O) = 2.30 Å

Cu	2.660764	8.232256	2.028897
Cu	4.079232	5.778272	2.296586
O	2.549547	6.466287	1.566879
O	4.198889	7.548686	2.749286
N	2.638924	10.039128	2.962802
H	3.370376	10.585492	2.483962
N	1.165033	8.922409	0.833409
H	0.318452	8.467436	1.205323
N	3.618477	3.799484	2.145999
H	3.670648	3.601504	1.135597
N	5.982775	5.220443	2.744160
H	6.040521	5.310058	3.769426
C	1.313556	10.621934	2.593601
H	1.277960	11.705938	2.819114
H	0.535592	10.126892	3.207559
C	2.978937	10.095125	4.471101
C	2.579735	11.471968	5.042335
H	1.484336	11.622044	5.099284
H	3.030360	12.307230	4.468004
H	2.966938	11.548028	6.077168
C	2.224593	8.965327	5.185198
H	1.123998	9.061041	5.085192
H	2.450106	8.996158	6.269160
H	2.538327	7.973424	4.803609

C	4.499097	9.920798	4.584613
H	4.799890	9.938867	5.649767
H	5.041666	10.743468	4.073106
H	4.820925	8.954521	4.150905
C	1.071749	10.385697	1.119645
H	0.084621	10.788608	0.819065
H	1.840519	10.902981	0.512933
C	1.228904	8.560579	-0.672295
C	0.265558	9.464526	-1.469080
H	0.229489	9.098945	-2.514097
H	0.588728	10.522422	-1.511459
H	-0.770602	9.417018	-1.074801
C	2.677130	8.742179	-1.148684
H	3.363886	8.060568	-0.606148
H	3.034126	9.785583	-1.030967
H	2.749237	8.502484	-2.227687
C	0.776928	7.099768	-0.800778
H	1.435388	6.428082	-0.215836
H	0.815706	6.789210	-1.862920
H	-0.271519	6.966294	-0.459602
C	4.759016	3.098906	2.810006
H	4.779658	2.024670	2.538960
H	4.614196	3.164586	3.906467
C	2.213170	3.340162	2.608171
C	1.233036	3.734950	1.495052
H	0.203590	3.441430	1.778116
H	1.471015	3.218242	0.541292
H	1.247097	4.829986	1.324836
C	1.882499	4.049276	3.928841
H	2.612571	3.813066	4.729521
H	0.892446	3.712873	4.293095
H	1.838226	5.148399	3.790547
C	2.197273	1.807988	2.786132
H	2.799250	1.461286	3.648265
H	2.534259	1.278235	1.871152
H	1.154007	1.487897	2.976298
C	6.050660	3.768425	2.397899
H	6.913141	3.280092	2.892047
H	6.202066	3.685273	1.303595
C	7.136384	6.076051	2.164413
C	7.218139	7.347470	3.019614
H	6.262932	7.905796	2.985672
H	8.020785	8.006980	2.636356
H	7.463463	7.109393	4.076339
C	6.807532	6.401281	0.700477
H	6.685557	5.488947	0.082450
H	7.636592	6.982593	0.251782
H	5.886970	7.015405	0.625538
C	8.466918	5.301817	2.272238
H	8.674259	4.973636	3.311144
H	9.290255	5.983156	1.980830
H	8.523161	4.425142	1.597955

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