

Supporting Information for the manuscript:

Supramolecular Control of Monooxygenase Reactivity in a Copper(II) Cryptate

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Chart S1

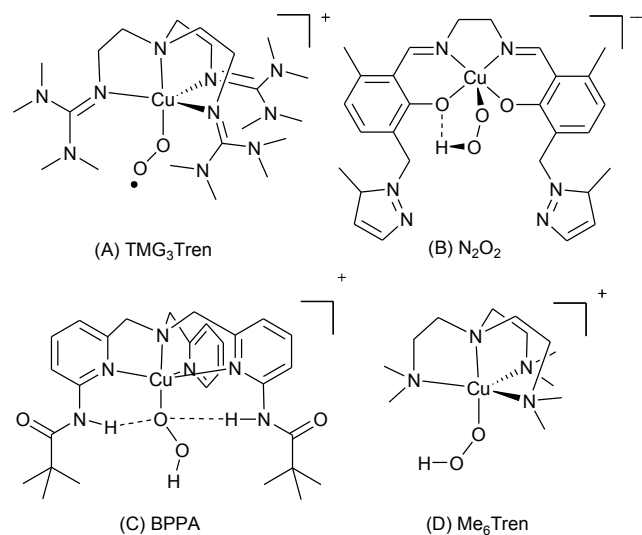


Chart S1. Well-characterized end-on mononuclear Cu/O₂ intermediates: $\text{TMG}_3\text{Tren-Cu(II)-superoxo}$,^{1,2} $\text{N}_2\text{O}_2\text{-Cu(II)-hydroperoxo}$,³ $\text{BPPA-Cu(II)-hydroperoxo}$,⁴ $\text{Me}_6\text{Tren-Cu(II)-Hydroperoxo}$.⁵

Figure S1

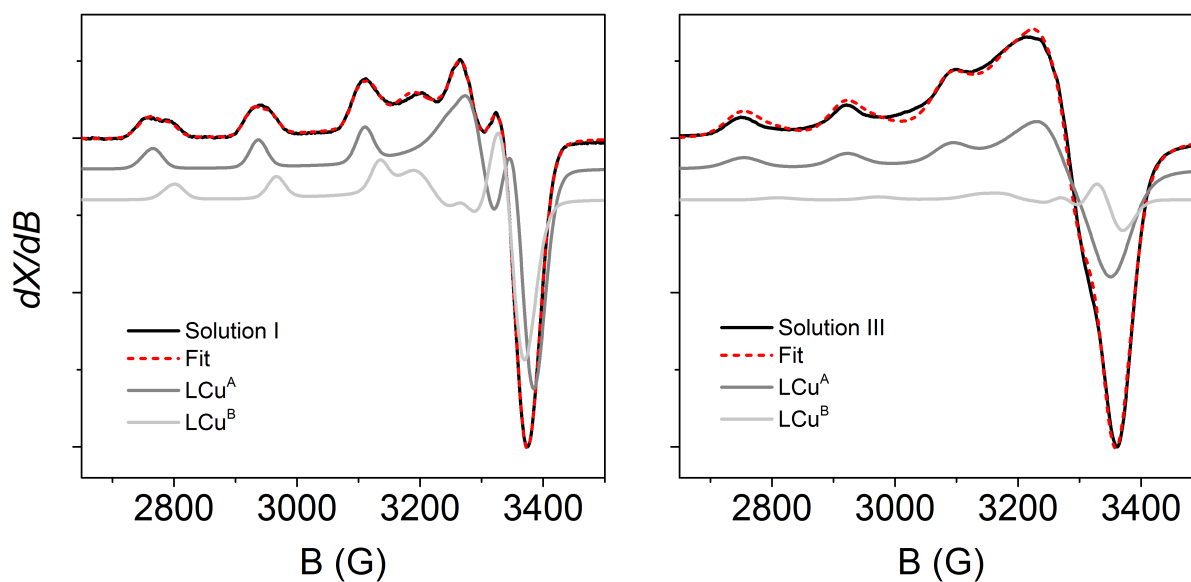


Figure S1. X-Band EPR spectra of solutions I and III in black, Easypin fit spectra in red and deconvolution of the fitted spectra in gray.

XYZ files

Figure S2 [LCu(η^2 -OAc)]⁺

103

CuC38N5H54O5

Cu	5.886205000	0.303054000	12.033788000
O	7.012581000	-0.678919000	13.342031000
O	5.489681000	-1.985521000	12.387034000
O	7.166522000	5.124849000	12.802208000
O	2.502170000	6.807445000	9.531625000
O	2.970795000	6.277365000	15.768489000
N	4.652306000	1.169670000	10.637981000
N	7.358449000	0.200143000	10.450582000
N	4.591400000	1.154464000	13.524839000
N	2.231428000	1.652217000	8.753200000
N	4.607246000	6.867649000	12.574102000
C	6.438888000	-1.839968000	13.198889000
C	6.940406000	-2.977212000	14.053656000
H	6.411770000	-2.957596000	15.018349000
H	8.012573000	-2.876540000	14.260541000
H	6.725220000	-3.937373000	13.571135000
C	5.578997000	1.725783000	9.614481000
H	6.064206000	2.603449000	10.058257000
H	5.032578000	2.066642000	8.721835000
C	6.632963000	0.692120000	9.239473000
H	6.162778000	-0.178878000	8.761602000
H	7.334591000	1.120107000	8.504455000
C	3.923776000	2.241952000	11.387100000
H	3.072137000	2.600890000	10.788234000
H	4.626533000	3.077844000	11.516462000
C	3.460032000	1.729123000	12.740305000
H	2.967727000	2.538017000	13.305315000
H	2.713828000	0.932382000	12.615465000
C	3.727991000	0.119212000	10.087523000
H	2.982376000	-0.086794000	10.863637000
H	4.296789000	-0.815164000	9.973166000
C	3.042425000	0.436851000	8.744060000
H	3.803183000	0.533707000	7.954678000
H	2.452251000	-0.467995000	8.477840000
C	7.758035000	-1.218021000	10.258499000
H	6.866341000	-1.847334000	10.163471000
H	8.329214000	-1.550935000	11.132067000
H	8.390664000	-1.323649000	9.359846000
C	4.090095000	0.114961000	14.456124000
H	3.331070000	0.522746000	15.142392000
H	4.930446000	-0.270693000	15.044506000
H	3.659962000	-0.709572000	13.876054000
C	0.908764000	1.435920000	9.342985000
H	0.367748000	2.389946000	9.391232000

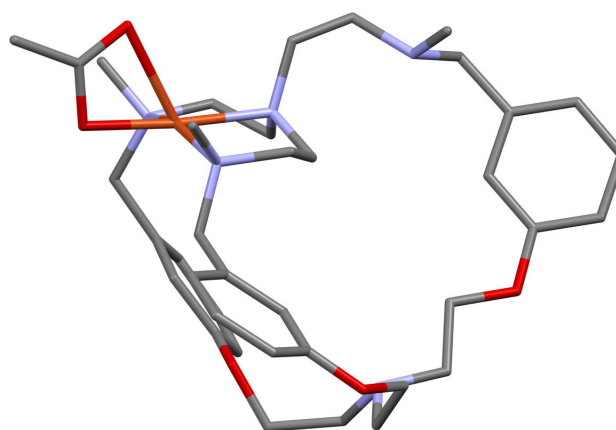


Figure S2

H	0.998971000	1.045117000	10.366632000
H	0.299593000	0.716963000	8.756756000
C	8.625728000	0.974716000	10.740633000
H	8.961363000	0.635186000	11.730729000
H	9.380953000	0.654052000	10.001539000
C	5.391453000	2.205136000	14.260907000
H	5.781007000	2.904929000	13.511535000
H	6.246571000	1.667367000	14.694910000
C	2.132123000	2.314208000	7.440266000
H	1.436969000	1.779746000	6.759158000
H	3.129279000	2.264761000	6.970336000
C	7.107340000	6.557854000	12.940759000
H	8.065064000	7.003912000	12.626529000
H	7.014574000	6.717419000	14.022881000
C	5.972498000	7.239269000	12.176801000
H	6.138340000	8.336795000	12.285390000
H	6.074035000	7.016705000	11.104345000
C	3.407074000	6.271332000	10.496445000
H	4.354540000	5.972498000	10.011036000
H	2.972964000	5.376213000	10.974161000
C	3.641783000	7.339838000	11.560869000
H	3.970974000	8.284219000	11.085239000
H	2.677334000	7.556870000	12.039955000
C	2.916464000	6.772564000	14.423565000
H	2.143254000	7.549945000	14.461460000
H	2.571299000	5.972756000	13.746409000
C	4.264060000	7.341256000	13.923701000
H	4.249476000	8.450692000	13.975309000
H	5.042906000	7.005078000	14.621860000
C	8.513261000	2.478448000	10.696550000
C	7.955402000	3.177390000	11.769453000
H	7.653158000	2.645111000	12.671603000
C	7.792584000	4.572759000	11.721188000
C	8.267609000	5.282332000	10.605389000
H	8.188681000	6.366808000	10.549763000
C	8.866384000	4.584499000	9.552834000
H	9.247761000	5.141531000	8.695885000
C	8.979971000	3.193830000	9.582098000
H	9.449160000	2.665939000	8.750167000
C	1.967847000	5.943140000	8.608037000
C	2.330194000	4.596915000	8.496767000
H	3.088877000	4.164382000	9.146339000
C	1.707815000	3.767262000	7.549464000
C	0.735143000	4.301408000	6.703192000
H	0.241650000	3.663987000	5.967154000
C	0.391824000	5.657414000	6.802184000
H	-0.369220000	6.073163000	6.140224000
C	0.995753000	6.479457000	7.746959000
H	0.723070000	7.530465000	7.844374000
C	3.507286000	5.037617000	15.985966000

C	4.135976000	4.260276000	15.001502000
H	4.272725000	4.654495000	13.991780000
C	4.666156000	2.998284000	15.328271000
C	4.574011000	2.529655000	16.644290000
H	5.014908000	1.570655000	16.918081000
C	3.944528000	3.310386000	17.620729000
H	3.877921000	2.946778000	18.646989000
C	3.411686000	4.554670000	17.301725000
H	2.925468000	5.174762000	18.055051000

Figure S3 $[\text{LCu}(\text{OAc})_{\text{eq}}(\text{MeOH})_{\text{ax}}]^+$

109

CuC39N5H58O6

Cu	5.723827000	0.166874000	11.903386000
O	7.084015000	-0.293532000	13.248492000
O	6.572062000	-2.475803000	13.578318000
O	7.120169000	4.864695000	12.835648000
O	2.612650000	6.945948000	9.581497000
O	2.896182000	6.128500000	15.767032000
O	4.734074000	-1.997195000	11.839120000
H	5.432491000	-2.293831000	12.525089000
N	4.505769000	1.104099000	10.482784000
N	7.178643000	0.034296000	10.317471000
N	4.405332000	1.001686000	13.378421000
N	2.122318000	1.839688000	8.603964000
N	4.666852000	6.771209000	12.653366000
C	7.252207000	-1.454554000	13.815606000
C	8.356227000	-1.510624000	14.854326000
H	7.939610000	-1.209276000	15.827461000
H	9.173090000	-0.820024000	14.614345000
H	8.728937000	-2.536000000	14.950383000
C	5.479836000	1.653426000	9.500522000
H	5.998500000	2.491023000	9.982299000
H	4.970555000	2.051934000	8.609815000
C	6.486814000	0.579028000	9.109684000
H	5.979125000	-0.259200000	8.611904000
H	7.215702000	0.985351000	8.389160000
C	3.814596000	2.175393000	11.268568000
H	2.996315000	2.603376000	10.668345000
H	4.553518000	2.968399000	11.453579000
C	3.301266000	1.616885000	12.585518000
H	2.804750000	2.410126000	13.168969000
H	2.552150000	0.834032000	12.408362000
C	3.535927000	0.147858000	9.853327000
H	2.784992000	-0.092066000	10.613609000
H	4.067052000	-0.792984000	9.657699000
C	2.870489000	0.587456000	8.533260000
H	3.639000000	0.688956000	7.752030000
H	2.235324000	-0.269167000	8.213417000
C	7.511837000	-1.398922000	10.122614000
H	6.590518000	-1.973708000	9.978457000
H	8.019877000	-1.777414000	11.016498000
H	8.175347000	-1.531953000	9.250102000
C	3.875626000	-0.059431000	14.268372000
H	3.109788000	0.336373000	14.953960000
H	4.699004000	-0.479530000	14.856510000
H	3.451717000	-0.859056000	13.650694000
C	0.790262000	1.659760000	9.185030000
H	0.296150000	2.635212000	9.279220000

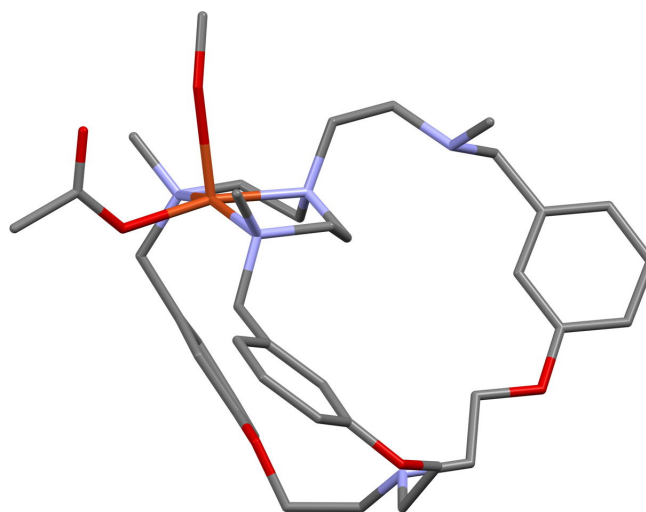


Figure S3

H	0.861130000	1.217146000	10.188675000
H	0.148100000	0.999863000	8.565453000
C	8.472885000	0.754613000	10.621861000
H	8.800739000	0.372791000	11.597456000
H	9.208902000	0.436554000	9.862535000
C	5.196936000	2.030086000	14.153022000
H	5.598503000	2.747824000	13.427234000
H	6.048801000	1.483206000	14.577817000
C	2.053340000	2.557505000	7.318284000
H	1.335790000	2.080468000	6.617719000
H	3.047777000	2.481227000	6.846394000
C	7.136356000	6.289761000	13.049533000
H	8.124414000	6.696518000	12.778634000
H	7.027914000	6.397430000	14.136801000
C	6.060098000	7.077149000	12.302205000
H	6.291197000	8.155505000	12.470160000
H	6.169577000	6.903496000	11.221585000
C	3.467714000	6.326541000	10.542081000
H	4.402721000	5.984464000	10.060947000
H	2.971317000	5.446232000	10.985286000
C	3.754042000	7.343364000	11.643240000
H	4.154819000	8.276858000	11.203564000
H	2.798498000	7.611502000	12.113637000
C	2.920223000	6.684813000	14.445603000
H	2.191992000	7.503988000	14.492746000
H	2.555468000	5.936984000	13.720952000
C	4.316271000	7.193848000	14.017323000
H	4.369345000	8.297341000	14.130926000
H	5.052057000	6.769985000	14.714207000
C	8.407828000	2.262225000	10.638655000
C	7.860074000	2.932970000	11.735941000
H	7.534156000	2.371326000	12.611942000
C	7.746028000	4.334077000	11.742790000
C	8.261449000	5.073651000	10.664960000
H	8.221376000	6.161581000	10.655619000
C	8.848959000	4.401097000	9.590131000
H	9.260379000	4.980306000	8.762264000
C	8.911959000	3.007085000	9.560655000
H	9.371061000	2.499000000	8.710769000
C	2.049230000	6.143220000	8.620785000
C	2.343965000	4.784469000	8.467038000
H	3.067941000	4.289471000	9.111582000
C	1.695610000	4.022871000	7.480920000
C	0.764791000	4.635671000	6.640490000
H	0.252345000	4.050467000	5.874739000
C	0.489760000	6.003275000	6.782925000
H	-0.237456000	6.481193000	6.124975000
C	1.120157000	6.759100000	7.765269000
H	0.900732000	7.818976000	7.896179000
C	3.368618000	4.856544000	15.945070000

C	3.986162000	4.092304000	14.943203000
H	4.161125000	4.519610000	13.952893000
C	4.460485000	2.799256000	15.230732000
C	4.316076000	2.282949000	16.524308000
H	4.714958000	1.298466000	16.770063000
C	3.690638000	3.047412000	17.515916000
H	3.581920000	2.645295000	18.524047000
C	3.217663000	4.324990000	17.236324000
H	2.738446000	4.934225000	18.002837000
C	4.173525000	-3.150266000	11.201698000
H	3.824066000	-3.881553000	11.947019000
H	4.899621000	-3.651811000	10.537243000
H	3.310624000	-2.834082000	10.598922000

Figure S4 [LCu(OOH)_{eq}]⁺

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CuC36N5H52O5

Cu	5.730305000	0.199833000	11.741252000
O	7.139813000	4.620606000	12.755846000
O	2.663057000	6.899194000	9.650286000
O	2.972966000	5.941066000	15.824458000
N	4.433057000	1.104275000	10.346152000
N	7.071363000	-0.012542000	10.056004000
N	4.392480000	0.899915000	13.234593000
N	2.036005000	1.846132000	8.531490000
N	4.727751000	6.602570000	12.705653000
C	5.373814000	1.665345000	9.341889000
H	5.915821000	2.488753000	9.824134000
H	4.841199000	2.086456000	8.475578000
C	6.364109000	0.596204000	8.888985000
H	5.841024000	-0.209217000	8.353702000
H	7.084533000	1.033704000	8.178398000
C	3.779090000	2.163038000	11.174050000
H	2.950127000	2.628148000	10.618532000
H	4.539677000	2.935158000	11.363380000
C	3.291193000	1.584739000	12.493245000
H	2.847739000	2.379544000	13.114270000
H	2.500084000	0.842525000	12.322494000
C	3.446181000	0.146395000	9.745484000
H	2.698029000	-0.070305000	10.516861000
H	3.961754000	-0.806964000	9.549602000
C	2.759211000	0.580721000	8.434872000
H	3.513658000	0.673344000	7.638849000
H	2.104750000	-0.265098000	8.126841000
C	7.290807000	-1.466061000	9.847330000
H	6.329134000	-1.966047000	9.674207000
H	7.746568000	-1.888208000	10.750557000
H	7.951030000	-1.645750000	8.980378000
C	3.847856000	-0.216862000	14.047160000
H	3.104901000	0.143159000	14.776525000
H	4.673048000	-0.710932000	14.570555000
H	3.365941000	-0.943291000	13.379267000
C	0.708396000	1.684658000	9.126967000
H	0.237026000	2.668621000	9.245591000
H	0.782621000	1.223235000	10.122051000
H	0.043130000	1.049962000	8.505343000
C	8.417578000	0.618766000	10.307620000
H	8.791471000	0.154248000	11.230532000
H	9.087890000	0.324041000	9.480174000
C	5.197758000	1.860562000	14.083282000
H	5.638471000	2.602263000	13.404423000
H	6.012527000	1.255234000	14.503611000
C	1.969075000	2.593897000	7.264142000

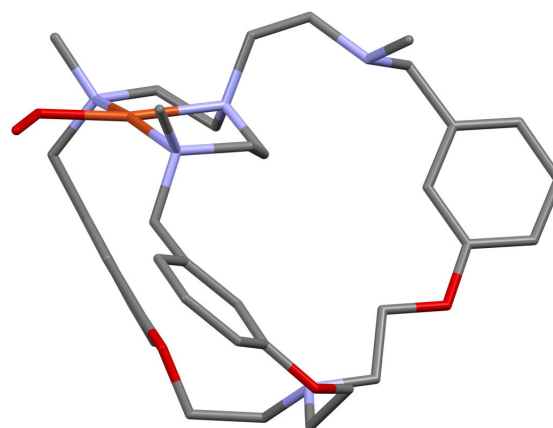


Figure S4

H	1.227972000	2.156399000	6.562131000
H	2.953863000	2.500932000	6.775116000
C	7.183729000	6.030351000	13.055712000
H	8.181572000	6.431403000	12.814643000
H	7.070242000	6.076392000	14.146913000
C	6.126304000	6.878238000	12.349054000
H	6.391337000	7.942596000	12.551709000
H	6.221569000	6.739430000	11.261888000
C	3.488836000	6.227448000	10.601242000
H	4.408322000	5.849652000	10.116500000
H	2.953039000	5.363554000	11.031897000
C	3.821086000	7.216886000	11.714803000
H	4.245551000	8.143521000	11.282969000
H	2.880540000	7.508829000	12.200991000
C	2.997664000	6.531217000	14.517268000
H	2.294954000	7.370006000	14.595678000
H	2.600495000	5.813159000	13.779610000
C	4.401601000	7.011848000	14.080602000
H	4.483130000	8.111835000	14.209267000
H	5.134738000	6.560478000	14.762724000
C	8.408034000	2.124130000	10.424175000
C	7.856067000	2.743347000	11.550031000
H	7.492514000	2.140113000	12.384630000
C	7.776343000	4.143177000	11.643809000
C	8.331144000	4.933748000	10.623363000
H	8.314730000	6.021090000	10.677161000
C	8.922783000	4.312242000	9.520653000
H	9.361791000	4.930022000	8.735980000
C	8.950281000	2.921018000	9.404627000
H	9.409499000	2.455399000	8.530678000
C	2.073474000	6.141264000	8.668142000
C	2.328599000	4.779762000	8.474212000
H	3.040306000	4.247929000	9.102518000
C	1.656063000	4.064962000	7.469121000
C	0.740649000	4.728807000	6.650720000
H	0.207237000	4.180752000	5.871843000
C	0.506025000	6.099229000	6.832871000
H	-0.209030000	6.616429000	6.191492000
C	1.160756000	6.808571000	7.834070000
H	0.972140000	7.870129000	7.996232000
C	3.412219000	4.652342000	15.961915000
C	4.023455000	3.912040000	14.939065000
H	4.216051000	4.370573000	13.965610000
C	4.465419000	2.598717000	15.183425000
C	4.291570000	2.035267000	16.453147000
H	4.662969000	1.031660000	16.663739000
C	3.672364000	2.777199000	17.466076000
H	3.540543000	2.339699000	18.456582000
C	3.234792000	4.076232000	17.230627000
H	2.761779000	4.667294000	18.015086000

O	6.991851000	-0.835467000	12.694577000
O	6.865633000	-1.029144000	14.117401000
H	7.718499000	-0.667879000	14.436449000

Figure S5 $[\text{LCu}(\text{OOH})_{\text{eq}}(\text{MeOH})_{\text{ax}}]^+$

105

CuC37N5H56O6

Cu	5.837191000	0.287100000	11.851545000
O	7.175655000	-0.630339000	12.836312000
O	7.145634000	4.803405000	12.791645000
O	2.635068000	6.912132000	9.615243000
O	2.932540000	6.055558000	15.818365000
N	4.522334000	1.154862000	10.443892000
N	7.195357000	0.105757000	10.179462000
N	4.500668000	1.000837000	13.339133000
N	2.130161000	1.832884000	8.591214000
N	4.678317000	6.714256000	12.693154000
O	7.055416000	-0.798825000	14.268672000
C	5.454674000	1.722066000	9.435774000
H	5.979744000	2.562019000	9.907802000
H	4.916795000	2.122203000	8.562801000
C	6.465406000	0.665199000	9.002532000
H	5.955585000	-0.167544000	8.497521000
H	7.170179000	1.097660000	8.272911000
C	3.846351000	2.209194000	11.258448000
H	3.003189000	2.644554000	10.700009000
H	4.586506000	3.004534000	11.431249000
C	3.377980000	1.635094000	12.586207000
H	2.905593000	2.421812000	13.196413000
H	2.616056000	0.861268000	12.423389000
C	3.554372000	0.174640000	9.849609000
H	2.803083000	-0.037289000	10.619129000
H	4.083963000	-0.776275000	9.688623000
C	2.876592000	0.578327000	8.526197000
H	3.637254000	0.670112000	7.735896000
H	2.238196000	-0.282308000	8.223491000
C	7.467017000	-1.342050000	9.991760000
H	6.519086000	-1.883802000	9.882297000
H	7.982040000	-1.719958000	10.882168000
H	8.098983000	-1.510991000	9.101554000
C	3.988190000	-0.113639000	14.175690000
H	3.214004000	0.236193000	14.877294000
H	4.823767000	-0.547589000	14.734831000
H	3.566921000	-0.883464000	13.516404000
C	0.805047000	1.661620000	9.188151000
H	0.314457000	2.639098000	9.280835000
H	0.886155000	1.227200000	10.194797000
H	0.152898000	0.998696000	8.581699000
C	8.518319000	0.788828000	10.415843000
H	8.907557000	0.358173000	11.348670000
H	9.198010000	0.497693000	9.594708000
C	5.275411000	2.003106000	14.164582000
H	5.697569000	2.743327000	13.472689000

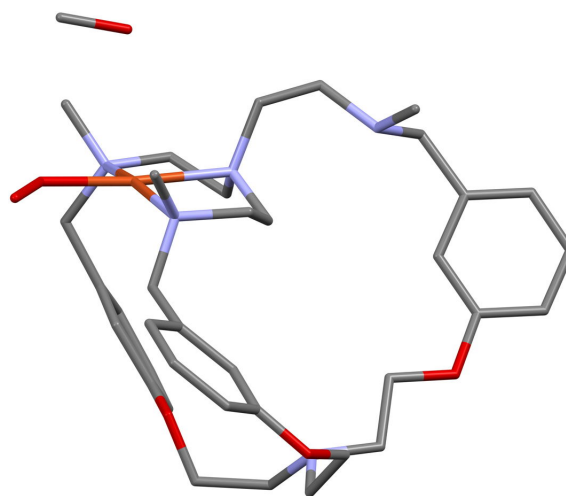


Figure S5

H	6.106351000	1.430991000	14.599179000
C	2.051680000	2.548338000	7.306712000
H	1.319091000	2.081115000	6.614692000
H	3.038295000	2.460357000	6.820269000
C	7.149279000	6.219551000	13.060305000
H	8.135674000	6.643603000	12.810644000
H	7.034064000	6.286075000	14.150279000
C	6.069611000	7.023343000	12.335727000
H	6.303111000	8.098509000	12.519372000
H	6.171560000	6.867281000	11.251640000
C	3.462894000	6.273936000	10.587579000
H	4.396310000	5.909207000	10.120187000
H	2.940505000	5.405158000	11.024288000
C	3.759170000	7.287779000	11.689378000
H	4.159303000	8.220207000	11.246722000
H	2.808094000	7.559336000	12.166950000
C	2.945536000	6.618475000	14.499149000
H	2.214667000	7.434728000	14.554913000
H	2.578582000	5.871557000	13.774581000
C	4.335623000	7.135013000	14.060096000
H	4.383500000	8.238933000	14.172337000
H	5.079493000	6.716408000	14.751561000
C	8.463676000	2.295387000	10.501042000
C	7.904457000	2.921891000	11.619193000
H	7.560035000	2.325598000	12.466272000
C	7.787750000	4.320608000	11.684646000
C	8.313824000	5.105343000	10.644708000
H	8.269962000	6.192663000	10.677851000
C	8.912779000	4.477764000	9.549358000
H	9.329270000	5.091102000	8.749049000
C	8.976237000	3.085856000	9.461108000
H	9.439371000	2.614220000	8.592528000
C	2.077607000	6.125547000	8.637095000
C	2.354067000	4.763544000	8.478483000
H	3.055920000	4.251664000	9.133949000
C	1.714063000	4.019012000	7.474178000
C	0.809470000	4.652967000	6.620593000
H	0.302194000	4.081611000	5.840978000
C	0.553016000	6.023512000	6.768272000
H	-0.153724000	6.517639000	6.099939000
C	1.175273000	6.762498000	7.768765000
H	0.968959000	7.824532000	7.903945000
C	3.408224000	4.782788000	15.983555000
C	4.043485000	4.039302000	14.977790000
H	4.225878000	4.482802000	13.995649000
C	4.520439000	2.743703000	15.248742000
C	4.357513000	2.201173000	16.529024000
H	4.754325000	1.212018000	16.759931000
C	3.715180000	2.945889000	17.525295000
H	3.592057000	2.524656000	18.523988000

C	3.242673000	4.227595000	17.263064000
H	2.750705000	4.820604000	18.034294000
O	4.472927000	-2.578672000	11.555557000
C	5.239131000	-3.488277000	12.376912000
H	5.611718000	-4.342674000	11.789562000
H	4.643611000	-3.864929000	13.223291000
H	6.087413000	-2.912410000	12.762891000
H	3.694461000	-3.063672000	11.232555000
H	7.880063000	-0.372080000	14.579752000

Figure S6 [LCu(OOH)_{eq}(OAc)_{ax}]

106

CuC38N5H55O7

Cu	5.784307000	0.051775000	11.820597000
O	7.247991000	-0.346552000	13.028887000
O	7.102938000	4.878765000	12.795870000
O	2.553245000	6.946682000	9.617846000
O	2.919248000	5.988712000	15.830735000
O	5.119517000	-2.017724000	12.049696000
N	4.515858000	1.076028000	10.384794000
N	7.280214000	0.073855000	10.193725000
N	4.453536000	0.960506000	13.337139000
N	2.113504000	1.903330000	8.531054000
N	4.605393000	6.730037000	12.685966000
O	6.811410000	-1.286008000	14.028559000
C	5.493553000	1.614694000	9.409273000
H	6.007797000	2.456242000	9.888831000
H	4.999019000	2.014359000	8.507824000
C	6.520141000	0.553736000	9.013113000
H	6.008282000	-0.319305000	8.584329000
H	7.192785000	0.958322000	8.233524000
C	3.898905000	2.148241000	11.214394000
H	3.084016000	2.647764000	10.664862000
H	4.678515000	2.899338000	11.412080000
C	3.379240000	1.598468000	12.537688000
H	2.881629000	2.404667000	13.106749000
H	2.616729000	0.829845000	12.352003000
C	3.502493000	0.167318000	9.756564000
H	2.736693000	-0.028441000	10.517551000
H	3.983401000	-0.811167000	9.580597000
C	2.848440000	0.634383000	8.446999000
H	3.617225000	0.741694000	7.666755000
H	2.195884000	-0.200432000	8.105928000
C	7.684741000	-1.341611000	10.022710000
H	6.795284000	-1.948883000	9.812585000
H	8.146743000	-1.681777000	10.957459000
H	8.413945000	-1.443389000	9.194963000
C	3.894862000	-0.095559000	14.207888000
H	3.132417000	0.301470000	14.901026000
H	4.717027000	-0.548983000	14.774614000
H	3.456006000	-0.875817000	13.575283000
C	0.802806000	1.738566000	9.154063000
H	0.321225000	2.718281000	9.273715000
H	0.906795000	1.286920000	10.150178000
H	0.129901000	1.087760000	8.553840000
C	8.531856000	0.845835000	10.478110000
H	8.892612000	0.464069000	11.445317000
H	9.280324000	0.577284000	9.707397000
C	5.270918000	1.944204000	14.123043000

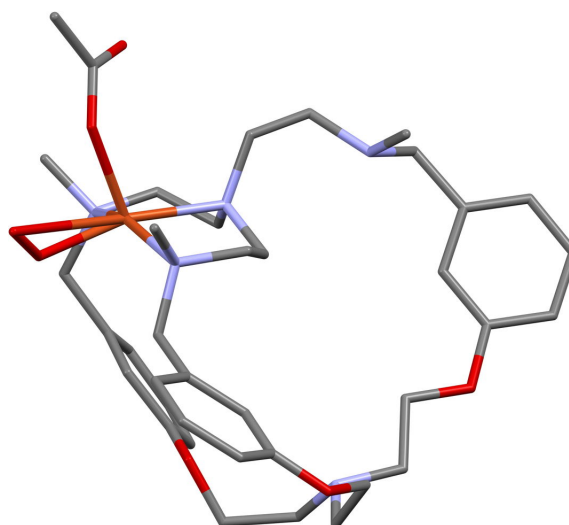


Figure S6

H	5.676645000	2.673920000	13.411840000
H	6.120128000	1.369064000	14.517809000
C	2.011655000	2.610712000	7.251176000
H	1.267483000	2.143750000	6.567593000
H	2.990496000	2.524313000	6.749541000
C	7.091508000	6.293095000	13.029845000
H	8.063377000	6.731163000	12.744794000
H	7.000924000	6.387411000	14.120692000
C	5.983786000	7.069745000	12.314951000
H	6.193132000	8.152273000	12.493534000
H	6.077151000	6.911679000	11.230604000
C	3.388276000	6.298408000	10.581528000
H	4.328242000	5.960157000	10.109317000
H	2.881561000	5.411526000	10.997437000
C	3.662217000	7.295317000	11.704446000
H	4.031108000	8.249572000	11.278380000
H	2.707383000	7.527803000	12.195972000
C	2.902281000	6.543102000	14.510738000
H	2.143341000	7.334560000	14.564217000
H	2.560431000	5.782394000	13.788291000
C	4.272056000	7.105026000	14.064876000
H	4.296495000	8.207569000	14.209022000
H	5.033240000	6.681906000	14.734205000
C	8.413111000	2.350364000	10.521155000
C	7.865909000	2.984933000	11.639672000
H	7.553916000	2.387670000	12.497760000
C	7.720544000	4.381227000	11.675888000
C	8.192974000	5.158160000	10.605888000
H	8.120694000	6.244600000	10.618224000
C	8.775215000	4.522043000	9.504788000
H	9.149176000	5.128224000	8.677846000
C	8.876482000	3.132219000	9.449956000
H	9.325686000	2.648995000	8.580423000
C	2.017552000	6.173596000	8.616808000
C	2.297035000	4.813900000	8.445038000
H	2.980066000	4.284953000	9.107569000
C	1.676653000	4.083009000	7.419562000
C	0.790237000	4.729876000	6.555383000
H	0.297166000	4.166693000	5.760478000
C	0.530842000	6.097976000	6.715877000
H	-0.162882000	6.601664000	6.040271000
C	1.132498000	6.823235000	7.739653000
H	0.922624000	7.883143000	7.887063000
C	3.436662000	4.723916000	15.992264000
C	4.054472000	3.985901000	14.972819000
H	4.194994000	4.421040000	13.980840000
C	4.563919000	2.700193000	15.231627000
C	4.455556000	2.170297000	16.523561000
H	4.875038000	1.187992000	16.743021000
C	3.836164000	2.910819000	17.536195000

H	3.757163000	2.495108000	18.542274000
C	3.326051000	4.180914000	17.281223000
H	2.846600000	4.770583000	18.063083000
C	4.829560000	-2.920013000	11.169443000
C	4.601728000	-4.325975000	11.730381000
H	5.537287000	-4.701793000	12.171310000
H	4.274803000	-5.013052000	10.941538000
H	3.854959000	-4.298406000	12.537196000
O	4.737465000	-2.727560000	9.937131000
H	6.322339000	-1.936701000	13.451406000

Figure S7 [LCu(OAc)_{eq}(OOH)_{ax}]

106

CuC38N5H55O7

Cu	5.660258000	-0.272327000	11.849324000
O	6.764385000	-1.435789000	13.071734000
O	8.030558000	0.289527000	13.773140000
O	7.077125000	4.863773000	12.861005000
O	2.583245000	6.927419000	9.581769000
O	2.788233000	6.071766000	15.782969000
N	4.468027000	0.965537000	10.503574000
N	7.302893000	0.065175000	10.284566000
N	4.377906000	0.891273000	13.532491000
N	2.179912000	1.860569000	8.517010000
N	4.589491000	6.739689000	12.681442000
C	7.703964000	-0.910676000	13.801452000
C	8.425682000	-1.894881000	14.717284000
H	9.027648000	-2.587667000	14.109818000
H	7.703530000	-2.504014000	15.278912000
H	9.085906000	-1.360419000	15.409588000
C	5.466545000	1.595928000	9.605558000
H	5.959131000	2.393342000	10.173375000
H	4.988011000	2.074550000	8.733946000
C	6.524944000	0.599052000	9.140422000
H	6.045506000	-0.251991000	8.634696000
H	7.180778000	1.083412000	8.392560000
C	3.791205000	1.979946000	11.367160000
H	2.958683000	2.449161000	10.818989000
H	4.529579000	2.767358000	11.574799000
C	3.285316000	1.394030000	12.684367000
H	2.670025000	2.156987000	13.202380000
H	2.620287000	0.542833000	12.476058000
C	3.493639000	0.093664000	9.775374000
H	2.690614000	-0.143827000	10.482444000
H	3.976113000	-0.877119000	9.583830000
C	2.930483000	0.604659000	8.439949000
H	3.752385000	0.747585000	7.721455000
H	2.311861000	-0.224580000	8.024827000
C	7.693056000	-1.339888000	10.036286000
H	6.791342000	-1.953190000	9.911807000
H	8.239628000	-1.721469000	10.906056000
H	8.336565000	-1.428740000	9.138055000
C	3.897148000	-0.155801000	14.449406000
H	3.115696000	0.206207000	15.143892000
H	4.743797000	-0.531410000	15.038702000
H	3.506854000	-0.993915000	13.859230000
C	0.847619000	1.672397000	9.087922000
H	0.352114000	2.645754000	9.201136000
H	0.917454000	1.208286000	10.080806000
H	0.206087000	1.024125000	8.451678000

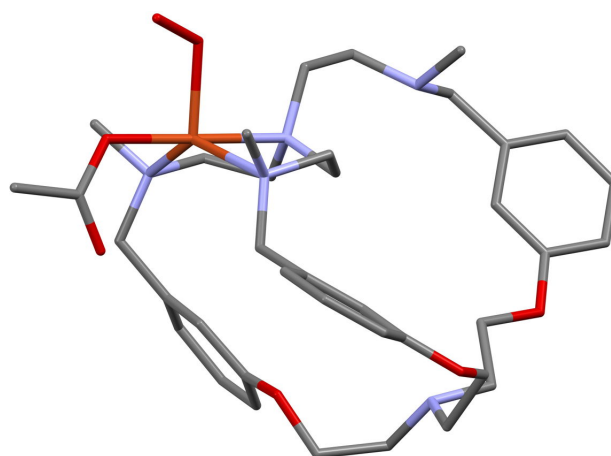


Figure S7

C	8.560818000	0.833785000	10.563558000
H	8.928741000	0.467105000	11.532236000
H	9.303859000	0.573136000	9.783464000
C	5.144766000	1.958194000	14.236615000
H	5.514932000	2.658886000	13.477849000
H	6.032237000	1.467533000	14.661264000
C	2.112955000	2.574677000	7.237781000
H	1.398740000	2.099186000	6.528685000
H	3.109428000	2.503989000	6.768981000
C	7.062029000	6.277430000	13.093336000
H	8.043928000	6.713277000	12.839837000
H	6.936498000	6.373194000	14.180650000
C	5.980899000	7.059699000	12.343498000
H	6.197798000	8.141640000	12.518213000
H	6.100075000	6.890529000	11.263512000
C	3.414729000	6.292811000	10.558872000
H	4.358204000	5.951309000	10.096320000
H	2.906359000	5.410545000	10.981901000
C	3.677737000	7.303841000	11.671154000
H	4.069144000	8.246528000	11.239335000
H	2.715032000	7.556237000	12.136465000
C	2.828118000	6.597004000	14.452625000
H	2.080224000	7.400770000	14.460506000
H	2.501596000	5.826353000	13.733622000
C	4.223018000	7.127832000	14.047642000
H	4.266586000	8.230422000	14.188743000
H	4.954589000	6.690995000	14.740514000
C	8.436257000	2.339187000	10.611820000
C	7.865317000	2.967845000	11.722831000
H	7.545770000	2.362498000	12.573598000
C	7.722380000	4.364749000	11.756822000
C	8.220585000	5.145241000	10.700567000
H	8.151205000	6.231788000	10.715588000
C	8.824065000	4.513127000	9.609180000
H	9.217183000	5.121369000	8.792577000
C	8.920691000	3.123186000	9.551303000
H	9.387423000	2.642064000	8.689520000
C	2.060843000	6.141093000	8.585940000
C	2.353117000	4.782041000	8.429204000
H	3.030587000	4.263439000	9.105778000
C	1.752940000	4.040587000	7.399608000
C	0.868789000	4.671567000	6.521711000
H	0.392050000	4.098235000	5.724115000
C	0.591954000	6.037415000	6.671619000
H	-0.100997000	6.529279000	5.986551000
C	1.177310000	6.775234000	7.695494000
H	0.956529000	7.834216000	7.833112000
C	3.292712000	4.807486000	15.990642000
C	3.918853000	4.032870000	15.003790000
H	4.075643000	4.432901000	14.000047000

C	4.421250000	2.755207000	15.309723000
C	4.293109000	2.270883000	16.618409000
H	4.711349000	1.298664000	16.879813000
C	3.660462000	3.044452000	17.597254000
H	3.566402000	2.662343000	18.615361000
C	3.158997000	4.307481000	17.294327000
H	2.671529000	4.924721000	18.049512000
O	4.436657000	-1.827723000	11.581508000
O	4.556077000	-2.835800000	12.583431000
H	5.516690000	-2.749547000	12.825746000

Figure S8

It was unclear if $LCu^{A/B}$ had a vacant binding site or if an acetate ion was coordinating in place of the solvent. To distinguish the two options excess sodium acetate was added to solution II. If $[LCu(OAc)(MeOH)]^+ \rightleftharpoons [LCu(OAc)]^+ + MeOH$ was the governing process then excess acetate would not affect the equilibrium. If $[LCu(OAc)(MeOH)]^+ + AcO^- \rightleftharpoons [LCu(OAc)_2] + MeOH$ was the governing process then excess acetate would drive the reaction to the right and the EPR spectrum would be dominated by one copper complex. From Figure S8, it was clear that NaOAc did not significantly affect the LCu^A to LCu^B ratio, thus further confirming our assignment and eliminating $[LCu(OAc)_2]$ as a plausible species.

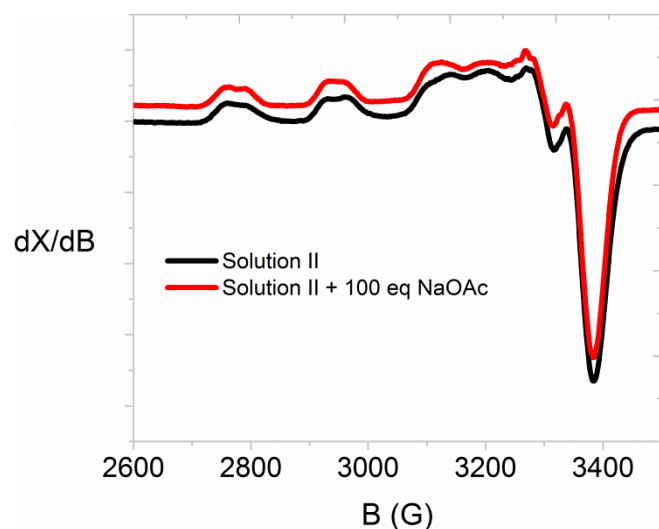


Figure S8. X-Band EPR spectra. Black: solution II. Red: Solution II + 100 equivalents of NaOAc.

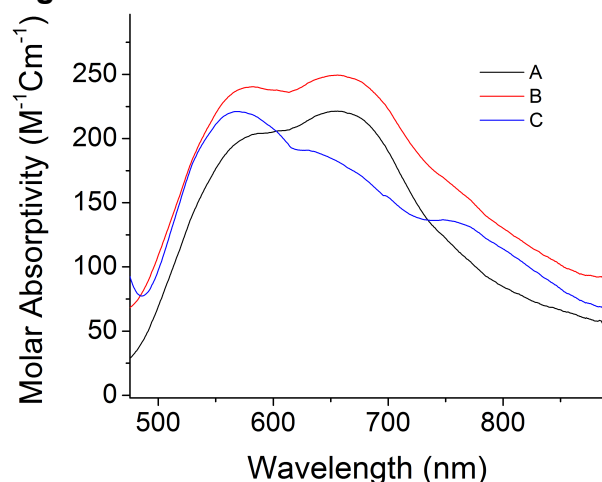
Figure S9

Figure S9. UV/Vis spectra at -50 °C in MeOH of Solution I (0.5 mM) and 10 equiv. Et_3N + 40 equiv. H_2O_2 . Zoom of the d-d transitions. Spectra have been smoothed. (A) 2.5 ms (B) 0.875 s and (C) 174.87 s.

Note S1

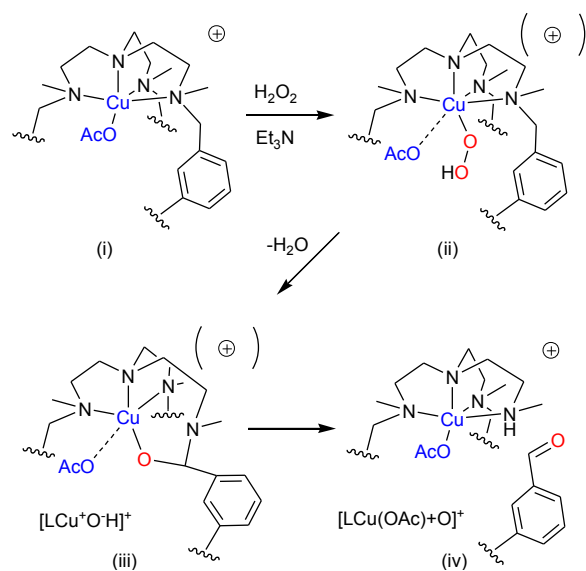
In the case of both L and L^{D} , if the dataset with 5 mM H_2O_2 is accounted for in the ANOVA test, the means are found to be statistically different. If the 5 mM dataset is considered to be an outlier, the means are found to be statistically similar. For the simplicity of the analysis, the means are considered statistically similar and 5 mM is considered an outlier. However, it should be noted that the decomposition may have small dependence on H_2O_2 when using 10 equivalents versus 20 or greater. Further stopped flow experiments would be needed to test this hypothesis but are not necessary for the general conclusions made in this publication.

Table S1

Table S1. Average rate of decomposition of $\text{LCu-OOH}^{\text{D}}$ and $\text{L}^{\text{D}}\text{Cu-OOH}^{\text{D}}$, the sample size (N) and the calculated KIE.

$[\text{H}_2\text{O}_2]$ (M)	N	k_{d} C-H (s^{-1})	N	k_{d} C-D (s^{-1})	KIE
0.005	5	$5.7 \pm 0.1 \times 10^{-02}$	5	$3.58 \pm 0.06 \times 10^{-02}$	1.60 ± 0.05
0.01	5	$6.6 \pm 0.2 \times 10^{-02}$	5	$4.0 \pm 0.2 \times 10^{-02}$	1.66 ± 0.05
0.015	5	$6.6 \pm 0.2 \times 10^{-02}$	5	$4.3 \pm 0.3 \times 10^{-02}$	1.52 ± 0.06
0.02	5	$6.6 \pm 0.1 \times 10^{-02}$	5	$4.7 \pm 0.5 \times 10^{-02}$	1.41 ± 0.05
Average KIE					1.5 ± 0.1

Scheme S1



Scheme S1. Previously proposed mechanism of the inner-sphere oxidation reaction of solution I with $\text{H}_2\text{O}_2/\text{Et}_3\text{N}$.

Figure S10

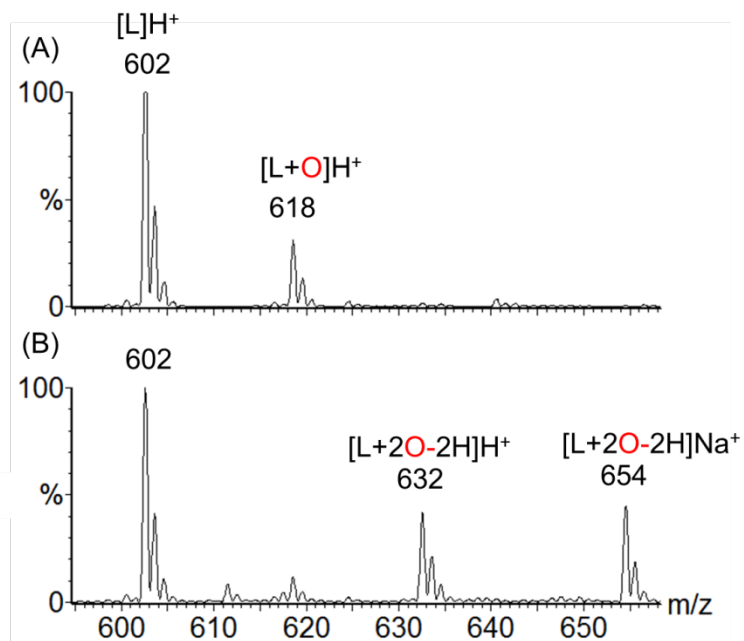


Figure S10. ESI-MS of the organic products after the reaction with 2 equiv. $\text{H}_2\text{O}_2/\text{Et}_3\text{N}$ and demetallation with (A) NH_4OH and (B) EDTA_{aq} .

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