

Electronic Supporting Information

Spectroscopic and Computational Characterization of Cu^{II}-OOR (R = H or Cumyl) Complexes Bearing a Me₆-tren Ligand

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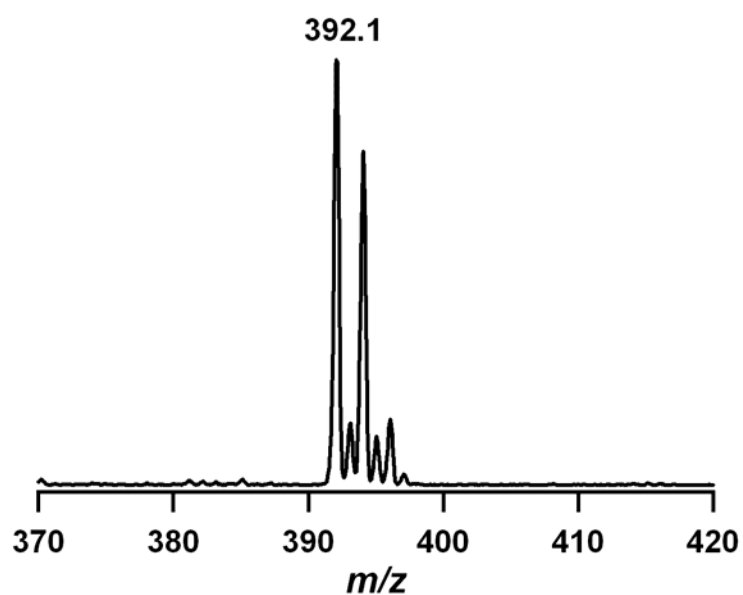


Fig. S1 ESI-MS of **1** in CH_3CN at room temperature.

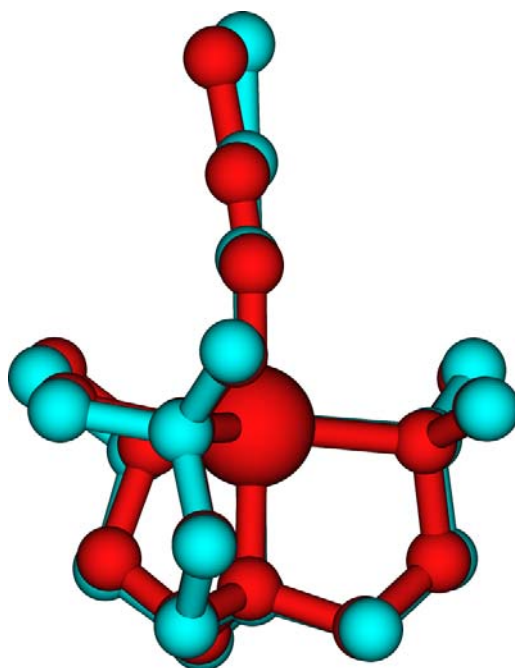


Fig. S2 An overlay of the crystal (red) and calculated (green) structures. The calculated RMS deviation is 0.13 Å. Hydrogen atoms are omitted for clarity.

Table S1. Distances and angles (Å and °). The isomer **3a** is presented in the main text.

	Cu-L _{ax}	Cu-N _{ax}	Cu-N _{eq1}	Cu-N _{eq2}	Cu-N _{eq3}	∠ N _{ax} -Cu-L _{ax}	∠ N _{eq} -Cu-N _{eq} ^a	O-O	∠ Cu-O-O
1	2.05	2.07	2.21	2.22	2.23	179.62	119.61	----	----
2	1.91	2.11	2.21	2.20	2.24	172.02	121.02	1.52	109.62
3a	1.92	2.13	2.22	2.20	2.25	171.60	120.86	1.52	109.25
3b	1.91	2.12	2.23	2.21	2.24	171.39	120.86	1.52	110.97
3c	1.91	2.14	2.25	2.23	2.21	170.32	120.07	1.51	109.41

^a The largest of the three N_{eq}-Cu-N_{eq} angles.

Table S2. Mulliken spin density distribution and relative energies (kcal/mol). The isomer **3a** is presented in the main text.

Complex	Cu	O _{inner}	O _{outer}	4xN	Rest	Rel. Energy
1	0.53	----	----	0.43	0.05	---
2	0.51	0.25	0.00	0.24	0.00	---
3a	0.51	0.26	-0.01	0.23	0.01	0.00
3b	0.51	0.26	-0.01	0.23	0.01	0.04
3c	0.50	0.26	0.00	0.23	0.01	-0.22

Coordinates in xyz-format

53
Cu-CNCH3
C 0.463539 1.022642 -2.854141
C -1.113181 -0.859004 -2.511356
C -1.821753 1.471984 -2.131989
C -0.154132 -1.934555 -2.016252
N -0.682084 0.501720 -2.036049
N -0.001649 -1.872797 -0.511594
C 2.457762 -1.482852 -0.257515
C 3.039285 0.966739 -0.090363
C 1.315778 -2.473775 -0.070370
Cu -0.001598 0.123486 0.036307
C -1.166901 -2.543198 0.184008
N 2.159787 -0.185014 0.442351
N -0.000403 2.095890 0.591683
C -0.002651 3.218061 0.914501
C -2.859248 -0.085822 1.145611
C -0.005688 4.615982 1.318293
N -1.482182 -0.499350 1.576411
C -1.347812 -1.997485 1.594969
C 2.384574 -0.304130 1.921581
C -1.218854 0.062584 2.941841
H -1.947816 -0.322402 3.667432
H -0.215577 -0.208689 3.271818
H -1.304065 1.149253 2.907268
H -3.610167 -0.429908 1.869673
H -2.905561 1.002778 1.084052
H -3.101499 -0.067739 0.169265
H -1.496180 2.447318 -1.768634
H -2.154089 1.549153 -3.173078
H -2.660327 1.125253 -1.527215
H 0.156339 1.171287 -3.898088
H 0.791592 1.980048 -2.445780
H 1.300292 0.322976 -2.835783
H 2.798424 1.842717 0.414816
H 4.097709 0.674910 0.088378
H 2.880031 1.026138 -1.162560
H 2.099533 0.631477 2.405669
H 1.787287 -1.116046 2.338605
H 3.442883 -0.504253 2.136921
H 1.505275 -3.393828 -0.638493
H 1.221078 -2.760242 0.978858
H 3.395556 -1.918738 0.115731
H 2.611680 -1.259661 -1.317143
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H -0.508802 -2.932109 -2.306515
H 0.834658 -1.805095 -2.460740
H -1.171046 -0.885990 -3.608841
H -2.125315 -1.035229 -2.136118
H 0.577030 5.219893 0.614075
H -1.029525 5.004920 1.344186
H 0.432884 4.727405 2.316078

50
Cu-OOH
Cu -0.003622 0.119904 0.059088
C 0.540088 1.018961 -2.820000
N -0.622066 0.509073 -2.029353
N -1.466695 -0.506174 1.576134
C -1.149669 0.092736 2.908865
C -1.080336 -0.830295 -2.510281
C -0.153596 -1.943564 -2.013772
N -0.005566 -1.909384 -0.516360
C -1.179036 -2.551871 0.173626
C -1.374122 -1.997662 1.587888
C -1.716119 1.524798 -2.084520
C 1.301790 -2.503821 -0.063775
C 2.468736 -1.530326 -0.256617
N 2.189330 -0.210387 0.381273
C 2.383217 -0.235118 1.860920
O -0.060896 1.869194 0.823774
C 3.036002 0.880458 -0.191954
C -2.810749 -0.023616 1.138409
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H -0.197816 -0.296296 3.272327
H -1.060525 1.173401 2.786366
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H -2.772856 1.063246 1.051477
H -3.075590 -0.448526 0.168256
H -1.340293 2.446880 -1.641426
H -2.026382 1.774765 -3.122581
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H 2.672009 1.838821 0.178661
H 4.091819 0.743652 0.086030

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H 2.021122 0.710997 2.266846
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H 3.445801 -0.362487 2.116620
H 1.499260 -3.441550 -0.603131
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H 3.390172 -1.983413 0.142641
H 2.643082 -1.349626 -1.321738
H -1.049017 -3.642978 0.209986
H -2.068107 -2.356491 -0.430984
H -2.271457 -2.448540 2.039455
H -0.527014 -2.268696 2.225001
H -0.531484 -2.923866 -2.337478
H 0.840517 -1.824709 -2.450529
H -1.134151 -0.859343 -3.609905
H -2.098124 -0.984424 -2.138185
O 0.577459 2.866175 -0.132627
H 0.105773 3.689334 0.126201

69
Cu-00cumene, (3a)
Cu 0.025612 0.130938 0.061350
C 0.602278 0.957388 -2.836282
N -0.575071 0.483093 -2.045134
N -1.457159 -0.469274 1.572825
C -1.133579 0.129876 2.902562
C -1.055727 -0.853068 -2.511901
C -0.157632 -1.977518 -1.994109
N -0.023969 -1.925995 -0.496759
C -1.218734 -2.531154 0.187644
C -1.406326 -1.962196 1.596335
C -1.651582 1.515049 -2.136452
C 1.260371 -2.555655 -0.029307
C 2.456900 -1.621335 -0.228274
N 2.211484 -0.288836 0.394014
C 2.398396 -0.302468 1.873573
C 3.078850 0.776222 -0.189812
C -2.783405 0.045283 1.118990
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H -2.079752 -0.981926 -2.147311
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O 0.580736 2.876423 -0.212425
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C 0.948204 5.113368 -0.868432
C -1.140357 4.508564 0.507748
C 1.143021 4.485940 1.586089
C 0.215116 6.115148 -1.527016
C 0.795729 6.871357 -2.552914
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C 2.855727 5.632477 -2.303029
C 2.278568 4.885196 -1.272736
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H 2.564734 7.219617 -3.740707
H 3.883278 5.442810 -2.597320
H 2.864215 4.119038 -0.777375
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H -1.709256 4.388972 -0.419067
H -1.500390 3.778304 1.234717
H 1.033468 5.517740 1.936438
H 0.766476 3.807941 2.356380
H 2.208511 4.290701 1.436433

69
Cu-00cumene, (3b)
Cu -0.012831 -0.004623 -0.011473
C 0.470404 0.806060 -2.929391
N -0.637192 0.193059 -2.138220
N -1.429054 -0.719649 1.522380
C -1.193056 -0.050174 2.836519
C -0.925882 -1.207987 -2.566353
C 0.095051 -2.189083 -1.983114
N 0.188970 -2.065445 -0.486579
C -0.939738 -2.781402 0.203740
C -1.213922 -2.195512 1.591687
C -1.842698 1.070132 -2.237948
C 1.528231 -2.512621 0.029795
C 2.607607 -1.454239 -0.205842
N 2.200112 -0.123342 0.337987
C 2.382508 -0.041609 1.817372
C 2.960980 0.988667 -0.306616
C -2.798164 -0.363671 1.041579
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C -1.186907 4.610781 0.568028
C 1.013015 3.999822 1.756448
C 1.052637 5.017590 -0.551760
C -1.731162 5.021804 1.794555
C -3.048335 5.493505 1.874267
C -3.845498 5.559607 0.728150
C -3.315296 5.151930 -0.502430
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H -3.921942 5.207462 -1.401192
H -1.599514 4.377184 -1.537313
H 1.097147 4.972567 2.251242
H 0.511383 3.302040 2.429615
H 2.027124 3.635695 1.564483
H 1.105334 6.038213 -0.159450
H 2.072185 4.638144 -0.674114
H 0.570957 5.055728 -1.531850

69
Cu-00cumene, (3c)
Cu -0.025459 0.160512 0.052779
C 0.590696 1.029516 -2.840160
N -0.573188 0.446763 -2.108177
N -1.560036 -0.590454 1.481514
C -1.381853 0.020895 2.831681
C -0.901683 -0.928238 -2.586757
C 0.067791 -1.962062 -2.009925
N 0.112952 -1.895720 -0.507644
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C -1.379731 -2.071481 1.504874
C 1.736701 1.375635 -2.239478
C 1.421548 -2.399198 0.035912
C 2.524284 -1.347236 -0.097471
N 2.122478 -0.047986 0.524680
C 2.251110 -0.079307 2.013382

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H -2.892839 0.899985 0.823380
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H -1.464768 2.323471 -1.775585
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C 1.284713 4.228107 1.625678
C 0.732056 5.172125 -0.703076
C -1.128125 4.701526 0.917995
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C 3.517341 4.632586 2.543068
C 3.126457 4.103635 3.776491
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C 0.906669 3.702380 2.877947
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H -0.038889 5.171942 -1.478321
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