Supplementary Material (ESI) for Dalton Transactions

Electronic Supporting Information

Spectroscopic and Computational Characterization of Cu^{II}-OOR (R = H or Cumyl) Complexes Bearing a Me_6-tren Ligand

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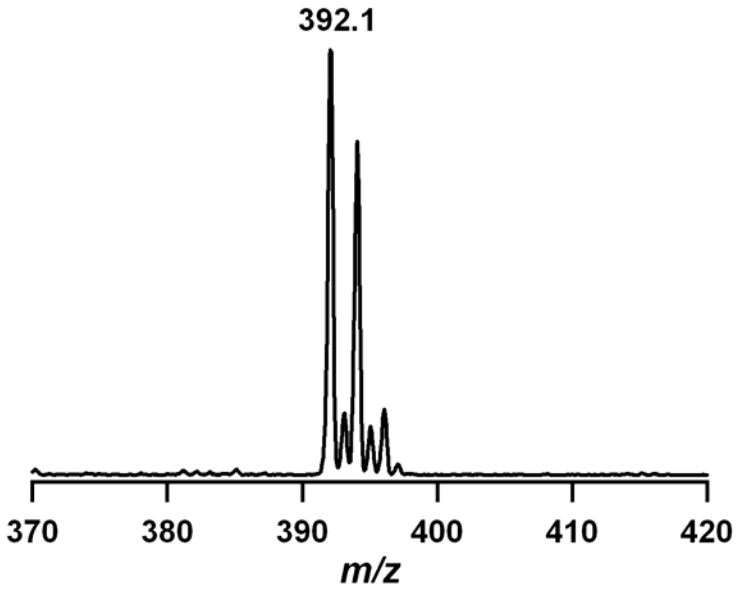

Fig. S1 ESI-MS of **1** in CH_3CN at room temperature.

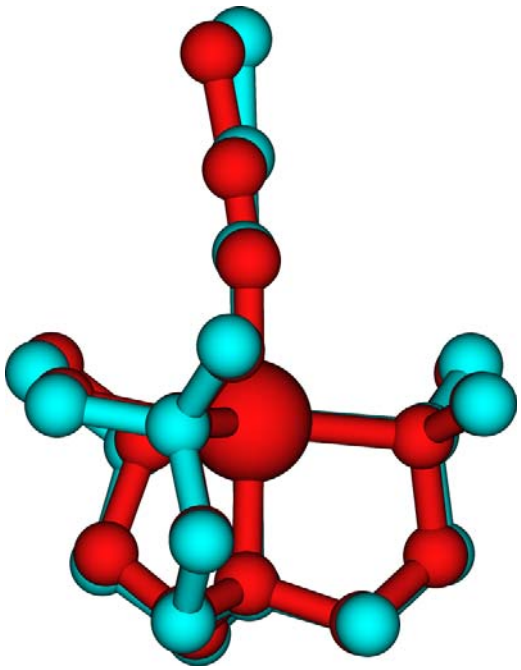

Fig. S2 An overlay of the crystal (red) and calculated (green) structures. The calculated RMS deviation is 0.13 Å. Hydrogen atoms are omitted for clarity.

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

```
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Cu-CNCH3
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 C -1.113181 -0.859004 -2.511356
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 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 0.906739 -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
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 H 0.432884 4.727405 2.316078


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 H -2.098124 -0.984424 -2.138185
 O 0.577459 2.866175 -0.132627
 H 0.105773 3.689334 0.126201


 69
Cu-OOcumene, (3a)
Cu 0.025612 0.130938 0.061350
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 H 1.033468 5.517740 1.936438
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 H 2.208511 4.290701 1.436433


 69
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Cu -0.012831 -0.004623 -0.011473
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 H 1.105334 6.038213 -0.159450
 H 2.072185 4.638144 -0.674114
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 69
Cu-OOcumene, (3c)
Cu -0.025459 0.160512 0.052779
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 N -0.573188 0.446763 -2.108177
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