Supporting Information

For

Hydroxo-Bridged Dicopper(II,III) and -(III,III) Complexes: Models for Putative Intermediates in Oxidation Catalysis

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Experimental Details

General. All reactions and manipulations were performed under an inert gas atmosphere using Schlenk techniques or Glove box unless otherwise noted. Water was distilled and degassed by one freeze–pump–thaw cycle. All chemicals were purchased from Aldrich and used without purification unless listed below. Acetylferrocenium hexafluoroantimonate was prepared as described in the literature.\(^1\) UV-vis spectra were collected on a HP8453 (199-1000 nm) diode array spectrophotometer. Elemental analyses were performed by Robertson Microlit Laboratory (Ledgewood, NJ). Infrared spectra were collected on a Nicolet Avatar 370 FT-IR equipped with a Smart OMNI Sampler. Perpendicular-mode X-band (9.62 GHz) EPR spectra were recorded on a Bruker Elexys E500 spectrometer. Simulations were performed using Bruker SimFonia software (version 1.25). GC-MS analysis was performed using an Agilent Technologies 7890A GC system and 5975C VL MSD. Electrospray ionization mass spectrometry (ESI-MS) was performed on a Bruker Bio-TOF II instrument. Cyclic voltammetry (CV) was performed in a three electrode cell with Ag/Ag\(^{+}\) reference electrode, platinum auxiliary electrode, and platinum working electrode and analyzed with BASi Epsilon software. Tetrabutylammonium hexafluorophosphate (Bu\(_4\)NPF\(_6\)) was used as the supporting electrolyte.

Variable-temperature magnetic susceptibility measurements of \(2\) were carried out under an applied dc field of 1 T using a Quantum Design Magnetic Properties Measurement System (MPMS) at the Institute for Rock Magnetism at the University of Minnesota (12.5 mg of finely ground crystalline material was used). The diamagnetic correction was estimated\(^2\) to be \(-400 \times 10^{-6}\) cm\(^3\)/mol. The interacting system was treated in terms of a \(S = 1/2, S = 1/2\) spin interaction Hamilton in its \(-2J\) form and theoretical molar susceptibilities were simulated using the fitting program julX.\(^3\) Paramagnetic impurities (PI) of \(~ 1\%\) are added to the simulation, and were obtained via the van Vleck-type equation without explicit Zeeman splitting.

X-ray Absorption Spectroscopy. Cu K-edge X-ray absorption spectra were measured at the Stanford Synchrotron Radiation Lightsource (SSRL) on the unfocused 20-pole, 2.0 T wiggler beam line 7-3 under storage ring parameters of 3 GeV and \(~500\) mA. A Rh-coated pre-monochromator mirror was used for harmonic rejection and vertical collimation. A Si(220) double-crystal monochromator was used for energy selection.

The samples \((~150 \mu L)\) were loaded into 2 mm Delrin XAS cells with 38 \(\mu m\) Kapton windows. The samples were maintained at a constant temperature of \(~10\) K during data collection using an Oxford Instruments CF 1208 continuous flow liquid helium cryostat. A Canberra solid-state Ge 30-element array detector was used to collect Cu K\(\alpha\) fluorescence data. Internal energy calibration was accomplished by simultaneous measurement of the transmission of a Cu-foil placed between two ionization chambers situated after the sample. The first inflection point of the foil spectrum was assigned to 8980.3 eV. Several rapid scans, from 8970 to 9020 eV, were collected for each sample and scans collected over time on the same spot revealed an isosbestic point at \(~8997.5\) eV. To properly conduct background subtraction and normalization of the data using PySpline,\(^4\) longer scans from 8675 to 9350 eV \((k = 9.5 \text{ Å}^{-1})\) were also collected. The longer scans were processed by fitting a second-order polynomial to the pre-edge region and subtracting this from the entire spectrum as a background. A one-region spline

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of order 2 was used to model the smoothly decaying post-edge region background, and normalization of the data was achieved by subtracting the spline and normalizing the edge jump to 1.0 at 9000 eV. Then, the pre-edge region of the shorter scans was processed to match the same region of the PySpline-processed longer scans, while the post-edge region of the shorter scans was normalized to match the intensity of the PySpline-processed longer scans at the isosbestic point. The background subtraction and normalization of the shorter scans were done using Igor Pro. Data represented here are the first scans of each short-scan data set to eliminate any spectral changes due to photoreduction.

\[ \text{H}_4\text{L}. \] A procedure modified relative to that previously reported was used.\(^5-7\) A solution of pyridine-2,6-dicarboxylidichloride (10 g; 0.049 mol) in dry \( \text{CH}_2\text{Cl}_2 \) (70 mL) was added drop-wise to a cooled (0 °C) solution of \( \alpha \)-phenylenediamine (5.3 g; 49 mol) and diisopropylethylamine (20 mL) in dry \( \text{CH}_2\text{Cl}_2 \) (20 mL). After the addition, the cooling bath was removed and the reaction mixture was stirred overnight at 20 °C. A white solid formed that was removed by filtration and washed with \( \text{CH}_2\text{Cl}_2 \) (2 × 10 mL). Methanol (720 mL) was added drop-wise to the filtrate to cause precipitation of a white solid, which was collected by filtration, washed with methanol (2 × 20 mL), Et\(_2\)O (2 × 25 mL), and dried in air to yield the crude product (4.91 g). The product was re-crystallized by dissolving in a minimum amount of boiling DMF, cooling to room temperature and then to 0 °C for 24 h. The resulting white crystals were collected by filtration, washed with DMF (20 mL), Et\(_2\)O (3 × 30 mL), and dried under a vacuum overnight to yield \( \text{H}_4\text{L}\cdot\text{DMF} \) (2.49 g, 18.5%). An additional batch of the product (1.21 g) was obtained by removal of solvent from the DMF filtrate and a second recrystallization as described above (total yield 3.69 g, 27.3 %).

\[ {^1}\text{H-NMR (DMSO-d}_6, 500 MHz) \delta (ppm): 10.965 (s, 4H, NH), 8.427-8.399 (m, 4H, CH\textsubscript{Ph}), 8.336-8.285 (dd, 2H, \textit{J}\textsubscript{HH} = 6.6 Hz, \textit{J}\textsubscript{H-H} = 8.7 Hz), 7.950 (s, 1H, H(CO)\textsubscript{DMF}), 7.850-7.819 (m, 4H, CH\textsubscript{Ph}), 7.416-7.384 (m, 4H, CH\textsubscript{Ph}), 2.887 (s, 3H, CH\textsubscript{3}DMF), 2.727 (s, 3H, CH\textsubscript{3}DMF). \]

Anal. Calcd for \( \text{C}_{26}\text{H}_{18}\text{N}_6\text{O}_4\text{·C}_2\text{H}_3\text{NO} \): C, 63.15; H, 4.57; N, 17.78; Found: C, 62.81; H, 4.61; N, 17.81.

\[ \text{NMe}_4[\text{L}\text{Cu}_2(\text{OH})] \] (2). \( \text{H}_4\text{L}\cdot\text{DMF} \) (180 mg, 0.33 mmol) was treated with 5 equiv. (0.66 mL) of a solution of \( \text{Me}_4\text{NOH} \) in \( \text{MeOH} \) (2.50 M). The mixture was heated to 60 °C to form a clear yellow solution, cooled to ambient temperature, and the solvent was removed \textit{in vacuo}. The residue was then dissolved in pyridine (7 mL). This solution was added dropwise over ~10 min to a solution of \( \text{Cu(OAc)}_2\cdot\text{H}_2\text{O} \) (152 mg, 0.80 mmol) dissolved in a water/pyridine mixture (6 mL, 1:2 v/v). The resulting dark green solution was stirred for 12 h, filtered, and the filtrate was treated with an aliquot (~20 mL) of a mixture of THF/Et\(_2\)O (1:4 v/v) to afford a green oily residue. Solvent was removed under reduced pressure and the resulting green powder was washed with boiling \( \text{CH}_2\text{Cl}_2 \) (4 × 5 mL) to remove the side product (\( \text{Me}_4\text{NOAc} \)). The residue was then dissolved in MeCN (50 mL) and filtered to yield a clear dark-green solution. Slow evaporation of this solution yielded a powder, which was collected by filtration, washed with dry DMF (2×5 mL), and dried \textit{in vacuo} to obtain the product as a brown powder (100 mg, 45%). Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a solution prepared by dissolving the brown powder in a minimum amount of distilled water (0.1 mL) that was subsequently diluted by an aliquot of acetonitrile (~3 mL). UV-Vis (DMF/H\(_2\)O) \( \lambda_{max} \) (e, M\(^{-1}\)cm\(^{-1}\)) : 570 (525). Positive ion ESI-MS (CH\(_3\)CN, \( m/z \) ): calcld 765.16 [M + \( \text{NMe}_4 \)]\(^+\), found 765.04. FTIR (solid, cm\(^{-1}\)) : 3573 (w), 3481 (w), 3034 (w), 1619 (s), 1600 (vs), 1572 (vs).

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1484 (s), 1438 (s), 1356 (vs), 1309 (m), 1240 (w), 1159 (w), 1080 (m), 1047 (w), 947 (w), 858 (w), 689 (s), 678 (s), 612 (m). Anal. Calcd for C$_{30}$H$_{27}$Cu$_2$N$_7$O$_5$: C, 52.02; H, 3.93; N, 14.15; Found: C, 51.52; H, 4.46; N, 14.17.

[NMe$_4$]$_2$[LCu$_4$(µ-O)] (1). Two solutions were mixed as for the preparation of 2, except using 9 equiv (1.18 mL) of Me$_4$NOH in MeOH (2.50 M). The reaction was performed similarly to that used for 2, except after allowing the solution in CH$_3$CN to slowly evaporate, X-ray quality dark green crystals formed. These crystals were collected by filtration and dried in vacuo to obtain the product (170 mg, 38%). UV-vis (DMF) $\lambda_{\text{max}}$ ($\varepsilon$, M$^{-1}$cm$^{-1}$): 580 (1225), 840 (70). ESI-MS (MeCN, m/z): calcd 607.95 [M–2(NMe$_4$)$_2$]$^2^−$, found 607.93 . FTIR (solid, cm$^{-1}$): 3392 (s), 3027 (w), 1667 (w), 1565 (vs), 1525 (m), 1480 (s), 1437 (w), 1369 (s), 1310 (m), 1074 (m), 1041 (w), 949 (s), 854 (w), 741 (m), 679 (s). EPR (9.64 GHz, DMF, 20K): see Figure S5.

Chemical oxidations of 2. A stock solution of 2 in H$_2$O/DMF (1:20) was prepared by first dissolving the powder form of 2 (13.9 mg, 10 mM) in ~0.1 mL of water. The mixture was sonicated for a few minutes and DMF was added in small portions (0.1 mL) to yield a green solution (2 mL, 10 mM). A 0.33 mL aliquot of this stock solution was mixed with DMF (2.7 mL) in a UV-vis cuvette and cooled to −50 °C. A solution of acetyl ferrocenium hexafluoroantimonate [(AcFc)(SbF$_6$)$_3$] in CH$_2$Cl$_2$ (0.23 mL, 14 mM) or (NH$_4$)$_2$Ce(NO$_3$)$_6$ (CAN) in CH$_3$CN (0.7 mL, 5 mM) was added, which immediately caused a color change to deep red (Figure S1). For titrations, the same procedure was used, except using smaller aliquots of oxidants added in incremental portions. Note that for the former, after the addition of the oxidant, the cuvette held 3.3 mL of a solution that was 1 mM in dicopper complex, whereas for the latter, the cuvette held 3.7 mL of a solution that was 0.5 mM in dicopper complex. The spectroscopic properties of the oxidized reaction solutions are discussed in the text and summarized as follows.

LCu$^\text{II}$Cu$^\text{III}$OH (3): UV-vis (DMF/H$_2$O) $\lambda_{\text{max}}$ ($\varepsilon$, M$^{-1}$cm$^{-1}$): 528 (2150), 1100 (1150). EPR (9.64 GHz, DMF/MeCN, 20K): $g_|| = 2.200$, $g_\perp = 2.050$, $A_||$(Cu) = 185 ×10$^{-4}$ cm$^{-1}$, $A_\perp$(14N) = 10 ×10$^{-4}$ cm$^{-1}$.

$L^A$Cu$^\text{III}$Cu$^\text{III}$OH$^-$ (4): UV-vis (DMF/MeCN/H$_2$O) $\lambda_{\text{max}}$ ($\varepsilon$, M$^{-1}$cm$^{-1}$): 525 (4785), 980 (2800).

Figure S1. Photographs in UV-vis cuvettes of (a) 1 mM solution of NMe$_4$[LCu$_2$(OH)] (2) in DMF, (b) product of oxidation by (AcFc)(SbF$_6$) (3) at −50 °C (1 mM), and (c) product of oxidation by CAN (4) at −50 °C (0.5 mM).
**X-ray crystallography.** All crystals were placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker SMART Platform CCD diffractometer for data collection. The data collections were carried out using MoKα radiation with a graphite monochromator (λ = 0.71073 Å) at 95 K. Structure solutions were performed by direct methods using SHELXS-97 software and refined against F² using full-matrix-least-squares using SHELXL-97 and SHELXL-2013 software. Data intensities were corrected for absorption and decay (SADABS). Final cell constants were obtained from least squares fits of all measured reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms in 2 were placed in ideal positions and refined as riding atoms with isotropic displacement parameters to be U(H)=1.2U_\text{eq}(C) for aromatic C atoms and U(H)=1.5U_\text{eq}(C) for alkyl C atoms (U_\text{eq}=1/3(U_{11}+U_{22}+U_{33}))$. The hydroxide hydrogen atom in 2 was located in the Fourier map and refined as a riding atom with relative isotropic displacement parameters. In 2 a solvent molecule (MeCN) was found to be disordered. The disorder was modeled as an occupation of the same position by one acetonitrile molecule and two water molecules. All disordered atoms were refined in an isotropic approximation. The final refined occupancies were 0.59, 0.32, and 0.09 for acetonitrile and two water molecules, respectively. In the acetonitrile molecule geometric restraints were used: 1.14(2) Å for C≡N and 1.47(2) Å for C-C bonds. Additionally, <C-C-N was restrained by using DANG instruction.

![Figure S2](image-url)  
**Figure S2.** Negative ion ESI-MS of [NMe₄]₂[LCu₄(µ₄-O)] (1) with inset showing experimental data (black) and simulation (blue) corresponding to [LCu₄(µ₄-O)]²⁻ (m/z 608).

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Figure S3. Positive ion ESI-MS of 2 with inset showing experimental data (black) and simulation (red) corresponding to $[\text{NMe}_4\text{LCu}_2(\text{OH}) + \text{NMe}_4]^+$ ($m/z$ 765).

Figure S4. Temperature dependence of the effective magnetic moment, $\mu_{\text{eff}}$, of NMe$_4$[LCu$_2$(OH)] (2) (shown as circles, 10–325 K). The black solid line represents the spin-Hamiltonian simulation. The parameters used for the fitting are: $S_{\text{tot}} = 1$, $g_1 = 2.20$, $g_2 = 2.05$, $2J = -11.5$ with a correction for the underlying diamagnetism of $-400 \times 10^{-6}$ cm$^3$/mol.
Figure S5. EPR spectrum of [NMe₄]₂[LCu₄(µ₄-O)] (1).

Kinetics of Decomposition of 3 and 4. The solutions of the 1-electron and 2-electron oxidized products 3 and 4 were prepared as described above at −20 °C. The decay of the chromophore was monitored in DMF in 5 second intervals until no further spectral changes were observed. The data were analyzed by the Olis Global Fitting software using a Singular Value Decomposition (SVD) algorithm and were fit to a first order decay processes (Figure S6). Reactions with dihydroanthracene were performed similarly, except the appropriate amount of DHA was added to the initial stock solution prior to addition of oxidant. Plots of $k_{obs}$ vs. [DHA] were fit to straight lines with nonzero intercepts, consistent with the rate law rate = $k$[DHA][complex] (Figure S7).
Figure S6. (Left) Change in the UV-vis spectrum of 3 (blue, top) and 4 (blue, bottom) in DMF (3) or DMF/CH$_3$CN (4) at -20 °C. Rate constants were determined by modeling the rate of decay of the blue curve. (Right) Representative deconvolution graph showing the contribution of each of the kinetic components to the total as a function of time. The black line represents the decay of 3 (top) or 4 (bottom) as the product forms (green line). The total calculated eigenvector (EV) contribution is given by the red line, with the blue line showing the experimental data. The calculated first order rate decay constants for 3 and 4 are $k = 3.1 \times 10^{-3}$ s$^{-1}$ and $2.3 \times 10^{-3}$ s$^{-1}$, respectively.

Figure S7. Plots of $k_{obs}$ vs. [DHA] for the decay of (a) 3 and (b) 4 in DMF at -20 °C with linear fits as indicated.

**XAS Spectroscopy.** Cu K-edge X-ray absorption spectroscopy was performed to directly probe for oxidation state of the Cu center in the complexes. The weak pre-edge transition observed before the onset of the rising edge corresponds to a dipole-forbidden, quadrupole-allowed 1s→3d transition. The energy position of this pre-edge transition is affected by the ligand field strength and the effective nuclear charge of the Cu center. Cu(III) compounds show a pre-edge shift of ~1.0–2.0 eV to higher energy as compared to analogous Cu(II) compounds. $^9$ Figure S7

$^9$ DuBois, J. L.; Mukherjee, P.; Stack, T. D. P.; Hedman, B.; Solomon, E. I.; Hodgson, K. O. *J. Am. Chem. Soc.* 2000, 122,
shows that 2 and the self-decay product of 4 have pre-edge features at ~8979.1 eV, which are characteristic of Cu(II) compounds. The energy position of the pre-edge of 4 is shifted by ~0.7 eV to higher energy relative to those of 2 and of the self-decay product of 4. For a given ligand system, the rising edge shifts to higher energy with increasing oxidation state. As shown in Figure S7, the rising edge maximum of 4 is shifted by ~1 eV to higher energy relative to those of 2 and of the self-decay product of 4. The shifts to higher energy observed in both the pre-edge and rising edge region indicate that 4 is an oxidized species relative to 2 and the self-decay product of 4 which are clearly Cu(II). The fact that the pre-edge shifts in 4 by ~0.7 eV suggests a highly covalent interaction of the oxidized Cu with its environment. Further XAS and EXAFS studies are underway.

**Figure S8.** Normalized Cu K-edge XAS spectra of 2 (black), 4 (red), and the self-decay product of 4 (green). The inset shows the smoothed second derivative spectra of the pre-edge region.
Theoretical Studies

The initial geometry for 2 was taken from the single crystal X-ray diffraction analysis measurement. Geometry optimizations were performed at the density functional level of theory (DFT) using the hybrid exchange-correlation PBE functional accounting for dimethylformamide (DMF) solvation effects using the IEF-PCM continuum solvent model. A mixed basis set generated from the EMSL basis exchange library and comprised of Def2-TZVPD for Cu atoms, 6-311+G(d,p) for N and O atoms, and 6-311G(d,p) for C and H atoms was used for the all calculations. The Hessian matrix was evaluated at each optimized geometry to confirm equilibrium structures as minima (no imaginary frequencies were predicted). Restricted singlet KS DFT wave functions were assessed for stability relative to an unrestricted, broken-symmetry, solution; such instability was observed for 2, and the optimization of its geometry was accomplished for the broken-symmetry (BS) singlet.

Time-dependent DFT (TD-DFT) calculations were performed using the PBE0 functional together with the SMD/DMF solvation model; solutions for the first 22 lowest states were computed. Redox properties were calculated using the M11-L functional and SMD/DMF solvation model (see below). All calculations were performed with the Gaussian09 suite of electronic structure programs. The calculated spectra and the nature of selected transitions are shown in Figure S8 and the table below this figure.

Gas phase Gibbs free energies and solvation free energies for the proton at 298K were based on experiment and taken to be -26.3 kJ/mol and -1112.5 kJ/mol, respectively. Also, for reactions in solution, standard free energies refer to a 1 M standard-state concentration for all species. Compared to the conventional 1 atm standard state for gas-phase calculations, this requires the introduction of a concentration-change term of RTln(24.5), which is equal to +7.9

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kJ/mol at 298 K.\textsuperscript{22} Thus, the total Gibbs energy for the proton in a 1 M solution after all corrections is equal to -1130.9 kJ/mol.

We consider electrochemical reactions of the form

\[ O_{\text{solv}} + n_e \cdot e_{(g)}^- \rightarrow R_{\text{solv}} \quad (\text{eq 1}) \]

\[ O_{\text{solv}} + n_e \cdot e_{(g)}^- + n_p \cdot H^+ \rightarrow R_{\text{solv}} \quad (\text{eq 2}) \]

where O is the oxidized species, R is the reduced species, ne is the number of electrons being transferred and np is the number of protons transferred. The Gibbs free energy change for proton coupled electron transfer was calculated using equation (eq 2), in all other cases equation (eq 1) was used.

The standard reduction potential of this class of reaction \( (E_{OR}^0) \) can be calculated using the equation

\[ E_{OR}^0 = -\frac{\Delta G_{OR}^0 - \Delta G_{\text{SHE}}^0}{n_e F} \]

where \( \Delta G_{OR}^0 \) is the standard state free energy of the redox reaction, F is the Faraday constant, and \( \Delta G_{\text{SHE}}^0 \) is the free energy change for the standard hydrogen electrode, which we take from experiment as 4.28 eV.\textsuperscript{23, 24} An additional \( n_p \cdot \text{pH} \cdot 0.0591 \text{V} \) term can be added to the potential to account for a pH different from 0.

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Figure S9. Experimental UV-vis and TDDFT data for (2) (top left), (3) (top right), (4) (bottom left), and (4-oxo) (bottom right). Experimental UV-vis spectra are given in black, TDDFT data are given in red, and simulated UV-vis spectra from gaussian broadened TDDFT data are given in blue.

Cu(II)OHCu(II)

Selected TD-DFT data for Cu(II)OHCu(II) obtained using PBE0/SMD(DMF) level of theory

| State Order | f     | Energy | Transition       | Coef   |
|-------------|-------|--------|------------------|--------|
|             |       | eV     | nm               | cm⁻¹   |        |
| 6           | 0.0054| 2.4226 | 511.77           | 19540  |        |
|             |       |        | 140A->157A       | -0.30361|
|             |       |        | 142A->157A       | -0.23671|
|             |       |        | 140B->157B       | -0.30364|
|             |       |        | 142B->157B       | -0.23674|
| 8           | 0.0178| 2.5565 | 484.98           | 20619.4|
|             |       |        | 139A->157A       | 0.20942 |
|             |       |        | 139B->157B       | 0.20946 |
| 17          | 0.0484| 3.2469 | 381.85           | 26188.3|
|             |       |        | 155A->157A       | 0.46581 |
|             |       |        | 155A->159A       | 0.24819 |
Frontier orbitals involved into mentioned above transitions.
**Cu(II)OHCu(III)**

TD-DFT data for Cu(II)OHCu(III) obtained using PBE0/SMD(DMF) level of theory

| State Order | f   | Energy   | Transition | Coef          |
|-------------|-----|----------|------------|---------------|
|             |     | eV       | nm         | cm⁻¹          |
| 1           | 0.0138 | 0.8119 | 1527.08 | 6548.45 | 153B->156B | 0.25618 |
|             |      |          |            |               | 155B->156B | 0.94836 |
| 2           | 0.0316 | 1.1453 | 1082.53 | 9237.62 | 152B->156B | -0.63258 |
|             |      |          |            |               | 153B->156B | 0.72277 |
|             |      |          |            |               | 155B->156B | -0.20313 |
| 3           | 0.0206 | 1.3622 | 910.2 | 10986.6 | 149B->156B | 0.31442 |
|             |      |          |            |               | 152B->156B | 0.46322 |
|             |      |          |            |               | 153B->156B | 0.39437 |
|             |      |          |            |               | 154B->156B | 0.65729 |
|             |      |          |            |               | 155B->156B | -0.2044 |
| 18          | 0.0396 | 2.5463 | 486.92 | 20537.3 | 131A->157A | -0.21125 |
|             |      |          |            |               | 142B->156B | 0.56633 |
|             |      |          |            |               | 147B->156B | -0.36998 |
|             |      |          |            |               | 148B->156B | -0.3584 |
Frontier orbitals involved into mentioned above transitions.
Cu(III)OHCu(III)

TD-DFT data for Cu(III)OHCu(III) obtained using PBE0/SMD(DMF) level of theory

| State Order | f   | Energy       | Transition | Coef       |
|-------------|-----|--------------|------------|------------|
|             |     | eV | nm | cm⁻¹ |               |            |
| 2           | 0.1092 | 1.4879 | 833.29 | 12000.6 |           | 150->156 | 0.21571 |
|             |       |     |     |     |            | 154->156 | -0.29409 |
|             |       |     |     |     |            | 155->157 | 0.54804 |
| 4           | 0.0306 | 1.7597 | 704.58 | 14192.9 |           | 153->156 | 0.66003 |
| 5           | 0.0228 | 1.9093 | 649.36 | 15399.8 |           | 152->156 | 0.6491  |

Frontier orbitals involved into mentioned above transitions.
Cu(III)OCu(III)

TD-DFT data for Cu(III)OCu(III) obtained using PBE0/SMD(DMF) level of theory

| State Order | f    | Energy | Transition | Coef   |
|-------------|------|--------|------------|--------|
|             |      | eV     | nm         | cm⁻¹   |
| 3           | 0.0242 | 1.8614 | 666.09     | 15013  |
|             |       |        | 151->157   | 0.5226 |
|             |       |        | 155->157   | 0.4174 |
| 4           | 0.0874 | 1.9634 | 631.48     | 15835.8|
|             |       |        | 150->157   | -0.23944|
|             |       |        | 151->157   | -0.39146|
|             |       |        | 153->156   | -0.22202|
|             |       |        | 155->157   | 0.45051|

Frontier orbitals involved into mentioned above transitions.
### Cartesian coordinates (Å)

Cartesian coordinates for all minima reported in the main text follow. Electronic energies at the SMD/M11-L ($\varepsilon_0$) and thermal contributions to 298 K free energy at the IEF-PCM/PBE0 ($G_{\text{corr}}$) are provided for each optimized structure.

(2) ($\varepsilon_0 = -4986.05280607$ a.u.; $G_{\text{corr}} = 0.317458$ a.u.)

| Atom | X-Coord | Y-Coord | Z-Coord | $\varepsilon_0$ | $G_{\text{corr}}$ |
|------|---------|---------|---------|----------------|-----------------|
| N    | 0.004184000000 | -2.624914000000 | 0.843667000000 | 0.843667000000 |
| N    | 0.004184000000 | 2.624914000000 | 0.843667000000 | 0.843667000000 |
| O    | -3.496128000000 | -2.643957000000 | 1.041504000000 | 1.041504000000 |
| O    | -3.496128000000 | 2.643957000000 | 1.041504000000 | 1.041504000000 |
| O    | 3.504212000000 | -2.638107000000 | 1.030177000000 | 1.030177000000 |
| O    | 3.504212000000 | 2.638107000000 | 1.030177000000 | 1.030177000000 |
| C    | 0.009310000000 | -4.425919000000 | 2.846262000000 | 2.846262000000 |
| C    | 0.009310000000 | 4.425919000000 | 2.846262000000 | 2.846262000000 |
| H    | 0.011387000000 | -5.155026000000 | 3.649233000000 | 3.649233000000 |
| H    | 0.011387000000 | 5.155026000000 | 3.649233000000 | 3.649233000000 |
| N    | -1.975727000000 | -1.429871000000 | -0.233428000000 | -0.233428000000 |
| N    | -1.975727000000 | 1.429871000000 | -0.233428000000 | -0.233428000000 |
| N    | 1.977732000000 | -1.426274000000 | -0.241174000000 | -0.241174000000 |
| N    | 1.977732000000 | 1.426274000000 | -0.241174000000 | -0.241174000000 |
| Cu   | 0.000824000000 | 1.328658000000 | -0.569678000000 | -0.569678000000 |
| Cu   | 0.000824000000 | -1.328658000000 | -0.569678000000 | -0.569678000000 |
| O    | 0.011895000000 | 0.000000000000 | -1.982585000000 | -1.982585000000 |
| H    | -0.849690000000 | 0.000000000000 | -2.412412000000 | -2.412412000000 |
| C    | -1.204328000000 | -3.958604000000 | 2.344060000000 | 2.344060000000 |
| C    | -1.204328000000 | 3.958604000000 | 2.344060000000 | 2.344060000000 |
| C    | 1.220106000000 | -3.955309000000 | 2.341080000000 | 2.341080000000 |
| C    | 1.220106000000 | 3.955309000000 | 2.341080000000 | 2.341080000000 |
| H    | -2.155888000000 | -4.293978000000 | 2.737406000000 | 2.737406000000 |
| H    | -2.155888000000 | 4.293978000000 | 2.737406000000 | 2.737406000000 |
| H    | 2.173714000000 | -4.288083000000 | 2.731232000000 | 2.731232000000 |
| H    | 2.173714000000 | 4.288083000000 | 2.731232000000 | 2.731232000000 |
| C    | -1.166186000000 | -3.027073000000 | 1.316972000000 | 1.316972000000 |
| C    | -1.166186000000 | 3.027073000000 | 1.316972000000 | 1.316972000000 |
| C    | 1.176778000000 | -3.023764000000 | 1.313532000000 | 1.313532000000 |
| C    | 1.176778000000 | 3.023764000000 | 1.313532000000 | 1.313532000000 |
| C    | -2.355607000000 | -2.346091000000 | 0.673597000000 | 0.673597000000 |
| C    | -2.355607000000 | 2.346091000000 | 0.673597000000 | 0.673597000000 |
| C    | 2.362016000000 | -2.340339000000 | 0.665090000000 | 0.665090000000 |
| C    | 2.362016000000 | 2.340339000000 | 0.665090000000 | 0.665090000000 |
| C    | -2.947154000000 | -0.707147000000 | -0.950250000000 | -0.950250000000 |
| C    | -2.947154000000 | 0.707147000000 | -0.950250000000 | -0.950250000000 |
| C    | 2.947176000000 | -0.705956000000 | -0.962269000000 | -0.962269000000 |
| C    | 2.947176000000 | 0.705956000000 | -0.962269000000 | -0.962269000000 |
| C    | -3.900355000000 | -1.381153000000 | -1.724589000000 | -1.724589000000 |
| C    | -3.900355000000 | 1.381153000000 | -1.724589000000 | -1.724589000000 |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | 3.898652000000000 | -1.380650000000000 | -1.736179000000000 |
| C       | 3.898652000000000 | 1.380650000000000 | -1.736179000000000 |
| H       | -3.885539000000000 | -2.465668000000000 | -1.723782000000000 |
| H       | -3.885539000000000 | 2.465668000000000 | -1.723782000000000 |
| H       | 3.884134000000000 | -2.465276000000000 | -1.735015000000000 |
| H       | 3.884134000000000 | 2.465276000000000 | -1.735015000000000 |
| C       | -4.843115000000000 | -0.696340000000000 | -2.474229000000000 |
| C       | -4.843115000000000 | 0.696340000000000 | -2.474229000000000 |
| C       | 4.839747000000000 | -0.696203000000000 | -2.489429000000000 |
| C       | 4.839747000000000 | 0.696203000000000 | -2.489429000000000 |
| H       | -5.570024000000000 | -1.246738000000000 | -3.062539000000000 |
| H       | -5.570024000000000 | 1.246738000000000 | -3.062539000000000 |
| H       | 5.565339000000000 | -1.246915000000000 | -3.079273000000000 |
| H       | 5.565339000000000 | 1.246915000000000 | -3.079273000000000 |

(3) \( (\epsilon_0 = -4985.87044819 \text{ a.u.}; G_{\text{corr}} = 0.317458 \text{ a.u.}) \)

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| N       | 0.079001000000000 | 2.710954000000000 | 0.812296000000000 |
| N       | -0.088930000000000 | -2.722642000000000 | 0.793658000000000 |
| O       | 3.577438000000000 | 2.638095000000000 | 1.021866000000000 |
| O       | 3.405885000000000 | -2.803232000000000 | 1.038459000000000 |
| O       | -3.406123000000000 | 2.923449000000000 | 0.880803000000000 |
| O       | -3.585284000000000 | -2.812959000000000 | 0.830804000000000 |
| C       | 0.130966000000000 | 4.688415000000000 | 2.644859000000000 |
| C       | -0.137807000000000 | -4.723462000000000 | 2.601836000000000 |
| H       | 0.153124000000000 | 5.486210000000000 | 3.378628000000000 |
| H       | -0.156660000000000 | -5.530207000000000 | 3.325952000000000 |
| N       | 2.026927000000000 | 1.386618000000000 | 0.812296000000000 |
| N       | 1.927347000000000 | -1.485339000000000 | -0.178464000000000 |
| N       | -1.940032000000000 | 1.433140000000000 | -0.130254000000000 |
| N       | -2.050850000000000 | -1.385521000000000 | -0.182704000000000 |
| Cu      | -0.025700000000000 | -1.321326000000000 | -0.503779000000000 |
| Cu      | 0.074935000000000 | 1.337729000000000 | -0.495238000000000 |
| O       | -0.040492000000000 | 0.029476000000000 | -1.881559000000000 |
| H       | 0.786768000000000 | -0.000955000000000 | -2.373784000000000 |
| C       | 1.325913000000000 | 4.124062000000000 | 2.203812000000000 |
| C       | 1.084380000000000 | -4.202630000000000 | 2.181595000000000 |
| C       | -1.094078000000000 | 4.230738000000000 | 2.162781000000000 |
| C       | -1.337337000000000 | -4.212929000000000 | 2.109344000000000 |
| H       | 2.287925000000000 | 4.450166000000000 | 2.578793000000000 |
| H       | 2.027964000000000 | -4.575779000000000 | 2.559424000000000 |
| H       | -2.035866000000000 | 4.645286000000000 | 2.499340000000000 |
| H       | -2.296626000000000 | -4.592731000000000 | 2.431513000000000 |
| C       | 1.261332000000000 | 3.109559000000000 | 1.259538000000000 |
| C       | 1.069896000000000 | -3.173646000000000 | 1.250913000000000 |
| C       | -1.076414000000000 | 3.206892000000000 | 1.228756000000000 |
\((4)\) \((\varepsilon_0 = -4985.68279008\ \text{a.u.}; \ G_{\text{corr}} = 0.320688\ \text{a.u.})\)
| Atom | X       | Y       | Z       | Coordinates |
|------|---------|---------|---------|-------------|
| C    | -1.205050000000 | 4.078284000000 | 2.309720000000 |
| C    | 1.220564000000 | -4.078970000000 | 2.310542000000 |
| C    | 1.220564000000 | 4.078972000000 | 2.310542000000 |
| C    | -1.205050000000 | 4.078972000000 | 2.310542000000 |
| C    | 1.220564000000 | -4.078970000000 | 2.310542000000 |

(4-oxo) \( \varepsilon_0 = -4985.22438589 \text{ a.u.}; G_{corr} = 0.310372 \text{ a.u.} \)

| Atom | X       | Y       | Z       | Coordinates |
|------|---------|---------|---------|-------------|
| N    | 0.000000000000 | 2.683681000000 | -0.872261000000 |
| N    | 0.000000000000 | -2.683681000000 | -0.872261000000 |
| O    | -3.488969000000 | 2.672926000000 | -0.927653000000 |
| O    | -3.488969000000 | -2.672926000000 | -0.927653000000 |
| O    | 3.488969000000 | 2.672926000000 | -0.927653000000 |
| O    | 3.488969000000 | -2.672926000000 | -0.927653000000 |
| C    | 0.000000000000 | 4.591153000000 | -2.757220000000 |
| C    | 0.000000000000 | -4.591153000000 | -2.757220000000 |

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