Supporting Information for:

Re-evaluating the Cu Pre-K-edge XAS Transition in Complexes with Covalent Metal-Ligand Interactions

Neil C. Tomson,* Kamille D. Williams, Xuliang Dai, Stephen Sproules, Serena DeBeer, Timothy H. Warren,* and Karl Wieghardt*

SI 1.1 Experimental details.

General Synthetic and Characterization Procedures and Instrumentation Details. All experiments were carried out in a dry nitrogen atmosphere using an MBraun glovebox and/or standard Schlenk techniques. 4A molecular sieves were activated *in vacuo* at 180 °C for 24 h. Diethyl ether and tetrahydrofuran (THF) were first sparged with nitrogen and then dried by passage through activated alumina columns. Pentane was first washed with conc. HNO_3 / H_2SO_4 to remove olefins, stored over $CaCl_2$ and then distilled before use from sodium/benzophenone. Benzene, toluene, fluorobenzene and ethylbenzene were purchased anhydrous and stored over 4A molecular sieves. All solvents (except fluorobenzene) were tested before use with a drop of sodium benzophenone ketyl in THF solution. All deuterated solvents were sparged with nitrogen, dried over activated 4A molecular sieves and stored under nitrogen. Celite was dried overnight at 200 °C under vacuum. ^{1}H, ^{13}C, and ^{19}F, NMR spectra were recorded on a Varian 400 MHz Spectrometer (400, 100.54, 376.14, respectively) at Georgetown. All NMR spectra were recorded at room temperature unless otherwise noted and were indirectly referenced to residual solvent signals or TMS as internal standards. Fluorobenzene (δ -113.15 ppm) in THF-d_8 was used as an internal standard for ^{19}F NMR experiments. UV-Vis spectra were measured at Georgetown on a Varian Cary 50 spectrophotometer, using air-tight cuvettes with a Teflon stopcock. Elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer at Georgetown. All reagents were obtained commercially unless otherwise noted. The recently reported $Ar^FN{=}NAr^F$ (Ar^F = 3,5-$(CF_3)_2C_6H_2$)[1] was prepared by a modification of the method reported for the synthesis of $C_6F_5N{=}NC_6F_5$[2] while [Me_2NN]Cu(ethylene)[3] was prepared according to literature procedures.

$Ar^FN{=}NAr^F$ (Ar^F = 3,5-bis(trifluoromethyl)phenyl). Adopted from synthesis of $C_6F_5N{=}NC_6F_5$.[2] 3,5-bis(trifluoromethyl)aniline (3.30 g, 14.0 mmol) and 10 % aqueous solution of NaOCl were mixed and stirred vigorously for 16 h. The organic component was extracted with three 40 mL portions of ether. The combined organic extracts were washed with water (5 × 30 mL) to remove all traces of chloride. The ether extracts were dried over $MgSO_4$ and concentrated to give an orange oil. Recrystallization from ethanol afforded 1.72 g (53 % yield) of orange crystals. Spectroscopic data match those reported by Takeda *et al.*[1]

[Me_2NN]Cu(η^2-$Ar^FN{=}NAr^F$) (3). A solution of $Ar^FN{=}NAr^F$ (0.110 g, 0.33 mmol) in 5 mL of toluene was added dropwise to a solution of [Me_2NN]Cu(ethylene) (0.130 g, 0.34 mmol) in 5 mL of toluene, the solution color changed from yellow to red-brown immediately. After stirred overnight, the volatiles were removed in vacuo and the residue was extracted with pentane (15 mL). The mixture was filtered through Celite, and the filtrate was concentrated and cooled to –35 °C to afford 0.180 g (78 %) red-orange crystals suitable for X-ray diffraction. ^{1}H NMR (THF-d_8, RT, 400MHz): δ 7.96 (s, 2H, *p*-H-diazene), 7.48 (s, 4H, *o*-H-diazene), 7.12 (m (broad), 6H, Ar-H), 5.03 (s, 1H, H-backbone), 2.46 (s, 6H, Me-backbone), 1.53 (s, 12H, Me-Ar) ^{13}C NMR (THF-d_8, RT): 165.21, 153.95, 148.44, 133.31, 132.56, 129.72, 126.07, 122.52, 97.72, 23.25 ^{19}F NMR (THF-d_8, RT): δ -62.03. Anal. Calc'd for $C_{37}H_{41}N_4F_{12}Cu$: C, 53.99; H, 3.80; N, 6.81. Found: C, 53.73; H, 3.77, N, 6.66.

Use of a non-arene solvent simplifies the solution characterization for [Me_2NN]Cu(η^2-$Ar^FN{=}NAr^F$) (**3**) since it appears that the electron-poor diazene may be displaced by an aromatic solvent such as benzene-d_6 to give free diazene $Ar^FN{=}NAr^F$ and the solvent species [Me_2NN]Cu(benzene).

Acquisition of X-ray absorption data. The compounds [Me_2NN]Cu(η^2-ONAr) (**2**),[4] [Me_2NN]Cu(η^2-CH_2=CHPh) (**4**),[3] and [Me_2NN]Cu(κ^2-O_2N_2Ar) (**5**)[4] (Ar = 3,5-$Me_2C_6H_3$) were prepared according to literature procedures. [Me_2NN]Cu(η^2-$Ar^FN{=}NAr^F$) (**3**) was prepared by addition of $Ar^FN{=}NAr^F$ [5] to [Me_2NN]Cu(η^2-CH_2=CH_2).[3] The Cu K-edge X-ray absorption spectra (XAS) of compounds **2**-**5** were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) at beamline 7-3 under ring conditions of 3 GeV and 60-100 mA. A Si(220) double-crystal monochromator was used for energy selection, and a Rh-coated mirror (set to an energy cutoff of 13 keV) was used for harmonic rejection. Incident and transmitted X-ray intensities were monitored using nitrogen-filled ionization chambers. X-ray absorption was measured in transmittance mode. During data collection, samples were maintained at a temperature of approximately 10 K using an Oxford Instruments liquid helium flow cryostat. Internal energy calibrations were performed by simultaneous measurement of the Cu reference foil placed between the second and third ionization chamber with the inflection point assigned at 8980.3 eV. Data represent five scan averages. The data were calibrated and averaged using EXAFSPAK.[6] Pre-edge subtraction and splining were carried out using PYSPLINE.[7] A three-region cubic spline of order 2, 3, 3 was used to model

the smooth background above the edge. Normalization of the data was achieved by subtraction of the spline and normalization of the post-edge region to a value of 1. X-ray absorption data from ref. XX was used in the analysis of [^{i}Pr$_2$NN]Cu(η^2-O$_2$) (**1**).

Data reduction and analysis. The intensities and energies of pre-edge features were determined by a procedure analogous to that reported previously.[8] Fits were performed over three energy ranges: 8976-8983, 8976-8984, and 8976-8985 eV. In addition to the initial pre-edge feature, a second, low-intensity feature was identified in the spectra for **2**, **3**, and **5**. These peaks were incorporated in the least-squares fits of the 8976-8985 eV energy range, then the parameters obtained for these additional spectral features were included, but held constant, during least-squares fits of smaller spectral ranges. The intense, rising-edge feature of **4** at 8984.3 eV was treated similarly. Two additional low-intensity features were observed in the spectrum of **5** at 8980.7 and 8983.3 eV, which correspond to the two low-intensity pre-edge transitions for compound **2**, the synthetic precursor to **5**. The higher-energy peak was treated as described above; line-shape parameters for the 8980.7 eV peak were included in all least-squares fits to the data. Plots of the second-derivatives of experimental data were smoothed using a three-point adjacent-averaging scheme.

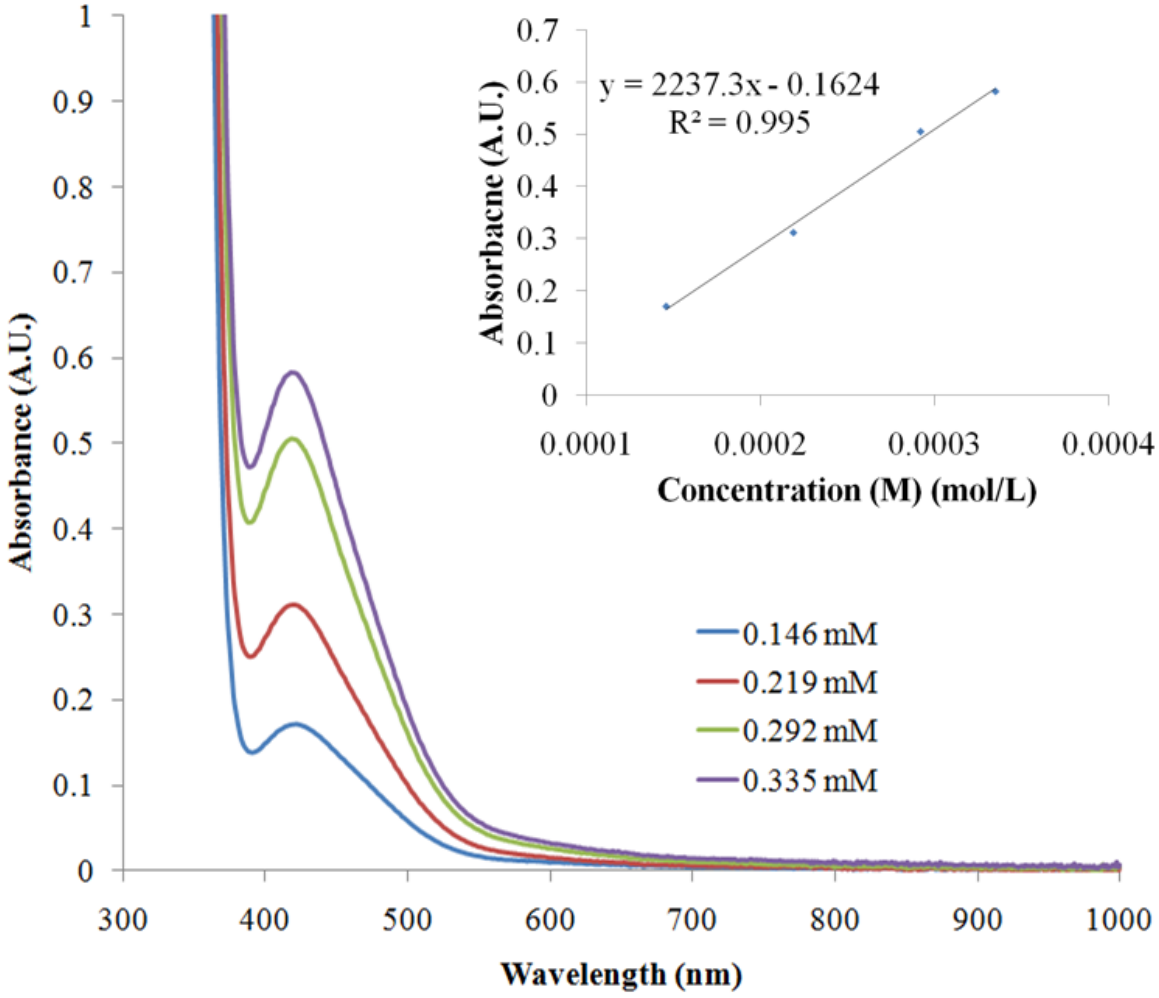
Computational Procedures. All DFT and *ab initio* calculations were performed with the ORCA electronic structure package.[9] The DFT calculations were carried out at the BP86 and B3LYP[10-12] levels of theory, using def2- variants of the all-electron Gaussian basis sets of split-valence (def2-SVP) and triple-valence (def2-TZVP) quality as developed by the Ahlrichs group.[13] The pure-DFT BP86 functional was used for geometry optimization calculations due to its superior performance in predicting geometric features; the hybrid-DFT functional B3LYP was used for subsequent calculations owing to its preferred use in predicting spectroscopic features. The calculations employed the resolution of identity (RI-J) algorithm for the computation of the Coulomb terms and the 'chain of spheres exchange' (COSX) algorithm for the calculation of the exchange terms.[14] For the fitting basis in the RI-J treatment, the 'def2' fit basis sets were used.[15]

The SCF calculations were tightly converged (1×10^{-8} E_h in energy, 1×10^{-7} E_h in the density change, and 5×10^{-7} in the maximum element of the DIIS error vector). In all cases the geometries were considered converged after *i*) the energy change was less than 1×10^{-6} E_h, *ii*) the gradient norm and maximum gradient element were smaller than 3×10^{-4} E_h-Bohr^{-1} and 1×10^{-4} E_h-Bohr^{-1}, respectively, and *iii*) the root-mean square and maximum displacements of all atoms were smaller than 6×10^{-4} Bohr and 1×10^{-3} Bohr, respectively. Geometry optimization calculations on the full molecules were carried out on redundant internal coordinates without imposing symmetry constraints. Truncated forms of complexes **1**-**6** were obtained as described in the text. Canonical orbital plots (electron density iso-surface threshold = 0.05) were generated with the program Molekel, *v*4.3.[16]

Time-dependent DFT (TD-DFT) calculations using the B3LYP functional were performed to predict the transitions in the pre-edge region of the Cu K-edge XAS spectra.[17,18] The basis-sets were chosen to match the basis sets used for the single-point ground state calculations, except for Cu, for which the CP(PPP) basis set[19] was implemented. The obtained Cu K-edge transition energies were shifted by a constant value of 195.55 eV to ease comparison with the experimental spectra.

MRCI calculations were performed by employing the state-averaged complete active space self-consistent field (SA-CASSCF) method for the calculation of the zero-order wavefunction. In individually selecting MRCI calculations, a test configuration was kept if its perturbation energy $H_{I0}^2/\Delta E$ was larger than a certain threshold T_{sel} (H_{I0} is the CI matrix element between the test configuration and muticonfigurational 0th order wavefunction; ΔE is the energy difference calculated with the Möller-Plesset (MP) 0th order Hamiltonian). The values reported below were obtained with $T_{sel} = 10^{-6}$ E_h. The energetic effects of unselected CSFs were estimated by second-order Rayleigh-Schrödinger theory using Möller-Plesset partitioning. We have employed the difference dedicated CI (MR-DDCI3) approach of Caballol, Malrieu and co-workers in this study.[20]

SI 1.2 Beer's law plot of [Me_2NN]Cu(η^2-Ar^FN=NAr^F) (3) in Et_2O at 25°C monitored at 421 nm.



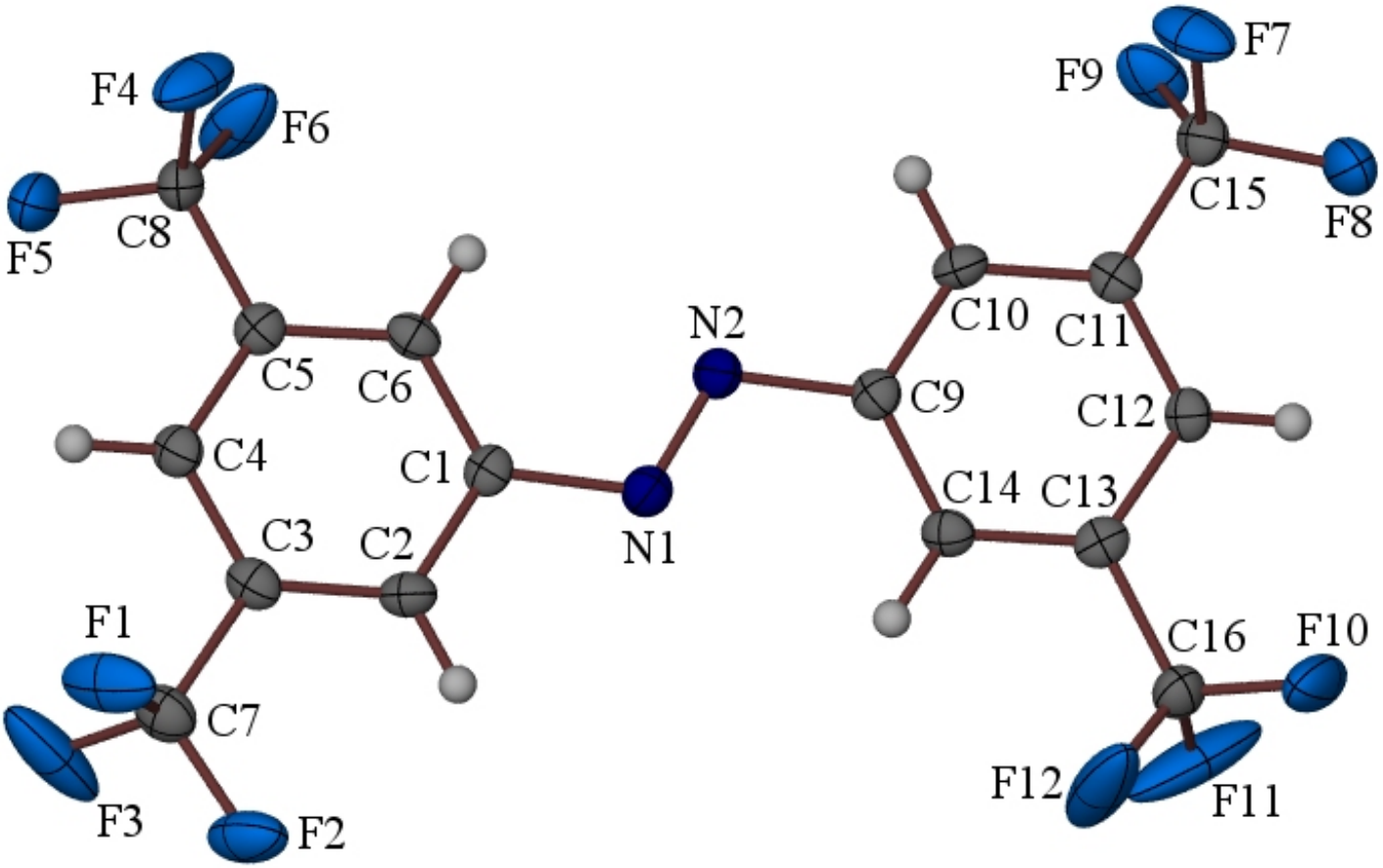
SI 1.3 Crystallographic details for [Me_2NN]Cu(η^2-Ar^FN=NAr^F) (**3**)

Single crystals of Ar^FN=NAr^F and [Me_2NN]Cu(η^2-Ar^FN=NAr^F) (**3**) were mounted under mineral or perfluoroalkyl ether oil on glass fibers in a cold nitrogen stream at 100(2) or 170(2) K on a Bruker SMART CCD system at Georgetown. Either full spheres (triclinic) or hemispheres (monoclinic or higher) of data were collected (0.3° or 0.5° ω-scans; $2\theta_{max} \geq 50°$; monochromatic Mo Ka radiation, l = 0.7107 Å) depending on the crystal system and integrated with the Bruker SAINT program. Structure solutions were performed using the SHELXTL/PC suite[a] and XSEED.[b] Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using Blessing's method as incorporated into the program SADABS.[c] Non-hydrogen atoms were refined with aniostropic thermal parameters and hydrogen atoms were included in idealized positions.

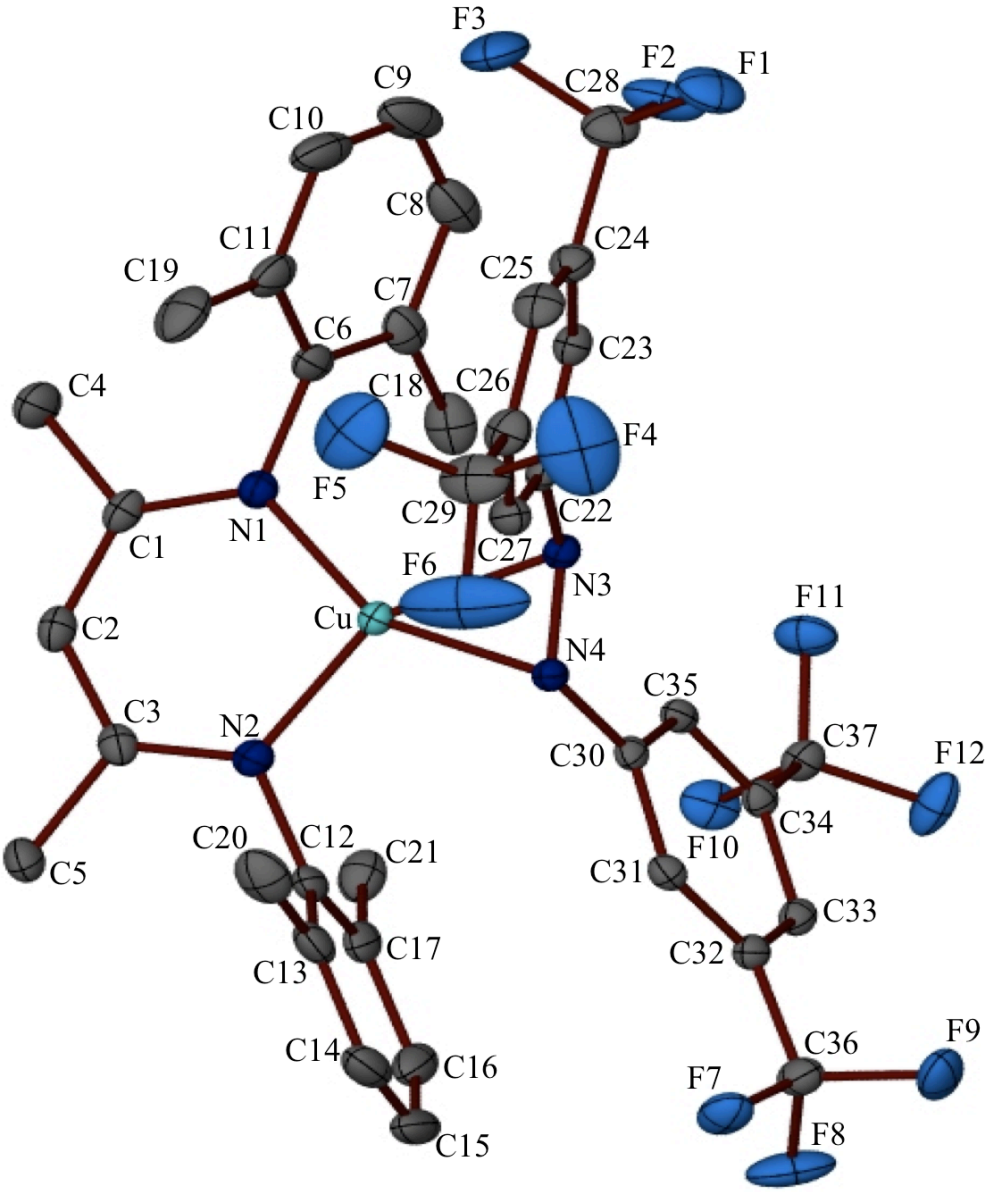
References for X-ray structure refinement details

(a) SHELXTL-PC, Vers. 5.10; 1998, Bruker-Analytical X-ray Services, Madison, WI; G. M. Sheldrick, SHELX-97, Universität Göttingen, Göttingen, Germany.
(b) L. Barbour, XSEED, 1999.
(c) SADABS-2008/1; G. M. Sheldrick, 1996, based on the method described in R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33; SADABS 2.06, 2002, Bruker AXS, Madison, WI; U.S.A.

SI 1.4 Labeled thermal ellipsoid diagram of $Ar^FN{=}NAr^F$. Selected bond distances (Å) and angles (deg): N1-N2 1.250(3), N1-C1 1.425(4), N2-CC9 1.424(4), N2-N1-C1 113.8(2), N1-N2-C9 113.7(2).



SI 1.5 Labeled thermal ellipsoid diagram of [Me_2NN]Cu(η^2-Ar^FN=NAr^F) (3) (all H atoms omitted). Selected bond distances (Å) and angles (deg): Cu-N1 1.8940(17), Cu-N2 1.8939(18), Cu-N3 1.9430(17), Cu-N4 1.9438(17), N3-N4 1.352(2), N3-C22 1.430(3), N3-C30 1.435(3), N1-Cu-N2 99.19(8), N3-Cu-N4 40.72(7), N1-Cu-N3 110.94(7), N1-Cu-N4 151.41(7), N2-Cu-N3 149.63(7), N2-Cu-N4 109.37(7), N4-N3-C22 111.73(11), N3-N3-C30 111.59(17).



SI 2. Experimental and calculated bond lengths for complexes **1**-**8**.

	Cu-L(1)		Cu-L(2)		L(1)-L(2)		Cu-N(1)$_{eq}$		Cu-N(2)$_{eq}$		Cu-N$_{ax}$	
	Exp.	*Calc.*	*Exp.*	*Calc.*	*Exp.*	*Calc.*	*Exp.*	*Calc.*	*Exp.*	*Calc.*	*Exp.*	*Calc.*
1[a]	1.821(5)	1.851	1.821(5)	1.850	1.392(12)	1.386	1.856(6)	1.889	1.856(6)	1.889	–	–
2[a]	1.851(3)	1.889 (O)	1.936(4)	1.985 (N)	1.333(4)	1.333	1.884(3)	1.910	1.886(3)	1.921	–	–
3	1.9430(17)	2.004	1.9438(17)	2.003	1.352(2)	1.347	1.8940(17)	1.931	1.8939(18)	1.931	–	–
4[a]	1.975(5)	2.005 (CH_2)	2.027(4)	2.080 (CHPh)	1.373(6)	1.398	1.913(3)	1.943	1.915(3)	1.946	–	–
5[a]	1.957(2)	2.015 (ONPh)	1.949(2)	1.996 (ON)	–	–	1.931(3)	1.963	1.929(3)	1.957	–	–
6[a]	1.84(1)	1.868	1.84(1)	1.868	1.22(3)[b]	1.361	1.99(2)	1.943	1.99(2)	1.943	2.25(2)	2.388
7^{+}[a]	1.992(5)	2.006 (CH_2)	2.022(5)	2.064 (CHPh)	1.395(6)	1.397	1.958(3)	1.968	1.973(3)	1.976	–	–
8	–	1.999 (C)	–	2.031 (N)	–	1.339	–	1.949	–	1.937	–	–
9	–	1.803	–	1.803	–	2.529	–	1.921	–	1.921	–	–

[a] Experimental data were obtained from the literature for **1**,[21] **2**,[4] **4**,[3] **5**,[4] **6**,[22] and **7**.[23]

[b] Literature reports suggest that the crystallographic data for **6** underestimate the O–O bond length.[24,25]

SI 3. DFT geometry optimization (BP86) and single-point (B3LYP) energies.

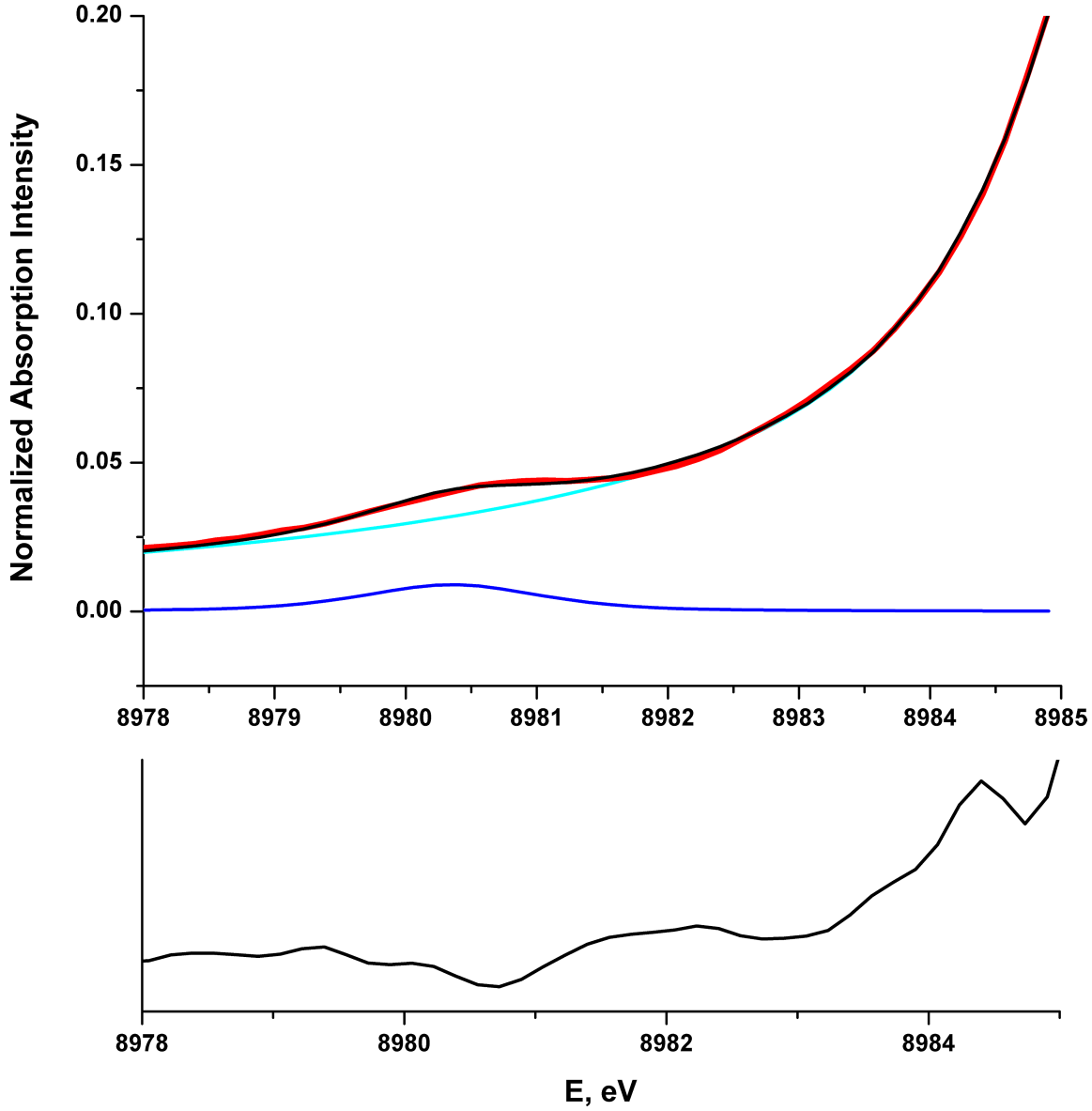
	BP86 / E_h	B3LYP[a] / E_h	B3LYP[b] / E_h
1	-2715.472644309	*-2714.437233263*	**-2714.407301229**
1'	-2479.775120322	*-2478.906007112*	–
2	-2926.515174733	*-2925.339267732*	**-2925.309100774**
2'	-2690.820071534	*-2689.808916759*	–
3	-4484.726122086	–	**-4482.845095174**
3'	-4249.033387676	–	**-4247.346918736**
4	-2874.560888803	–	**-2873.378891028**
4'	-2638.868327134	–	–
5	-3056.514729123	–	**-3055.246618293**
5'	-2820.820036190	–	–
6	–	–	**-3316.893921099**
6'	-2493.540883793	–	–
7^{+}	-2849.445594635	–	**-2525.836098772**[c]
8	-2890.607247358	*-2889.446512501*	**-2889.416680166**
κ^1-*N*-8	-2890.607715709	–	–
9	-2764.818009211	*-2763.785450238*	**-2440.925715141**

[a] Calculations performed with the *def2-TZVP* basis set on copper.

[b] Calculations performed with the **CP(PPP)** basis set on copper.

[c] Calculation performed on the crystallographic coordinates of the cationic portion of the molecule.

SI 4.1. Representative fit to the experimental spectrum (top; experimental in black; components of the fit in blue and cyan; sum of the fit in red) and 2nd derivative of the experimental spectrum (bottom) for complex **1**. Experimental data obtained from reference 26.

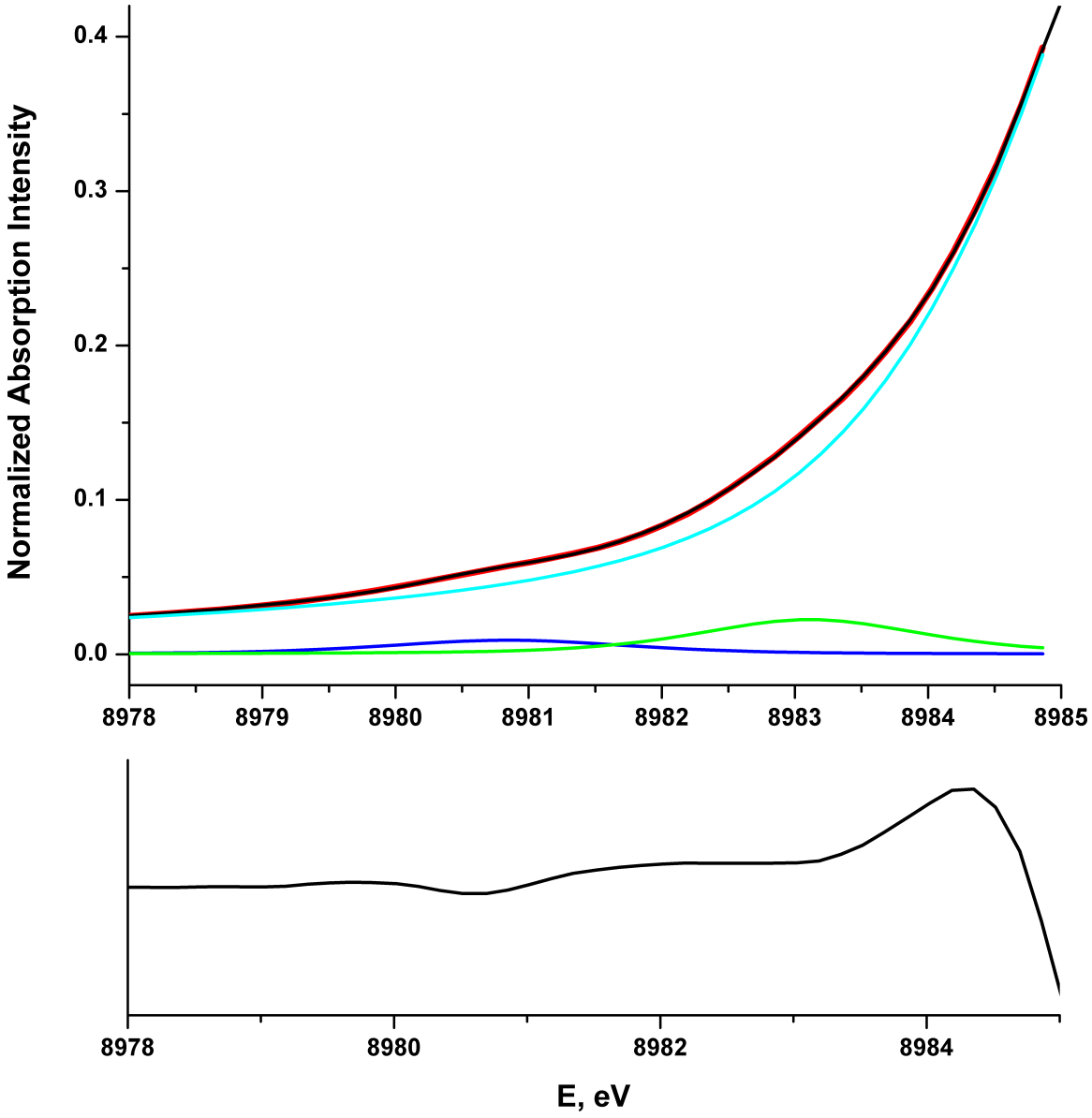


SI 4.2. Results of the fits to the initial pre-edge transition for **1**.

	Fit range / eV	Peak position / eV	Hwhm / eV	Peak height / au	Peak area[a]	Scaled peak area[b]
	8976-8983	8980.46	0.852	0.00966	0.017	1.7
	8976-8984	8980.44	0.850	0.00965	0.016	1.6
	8976-8985	8980.35	0.802	0.00903	0.015	1.5
Average		8980.42	0.835	0.00944	0.016	1.6
Standard deviation		0.06	0.03	0.00036	0.0011	0.11

[a] Peak area determined by multiplying the full-width at half-height by the peak height.
[b] Scaled peak area is equal to the peak area multiplied by 100.

SI 4.3. Representative fit to the experimental spectrum (top; experimental in black; components of the fit in blue, green, and cyan; sum of the fit in red) and 2nd derivative of the experimental spectrum (bottom) for complex **2**.

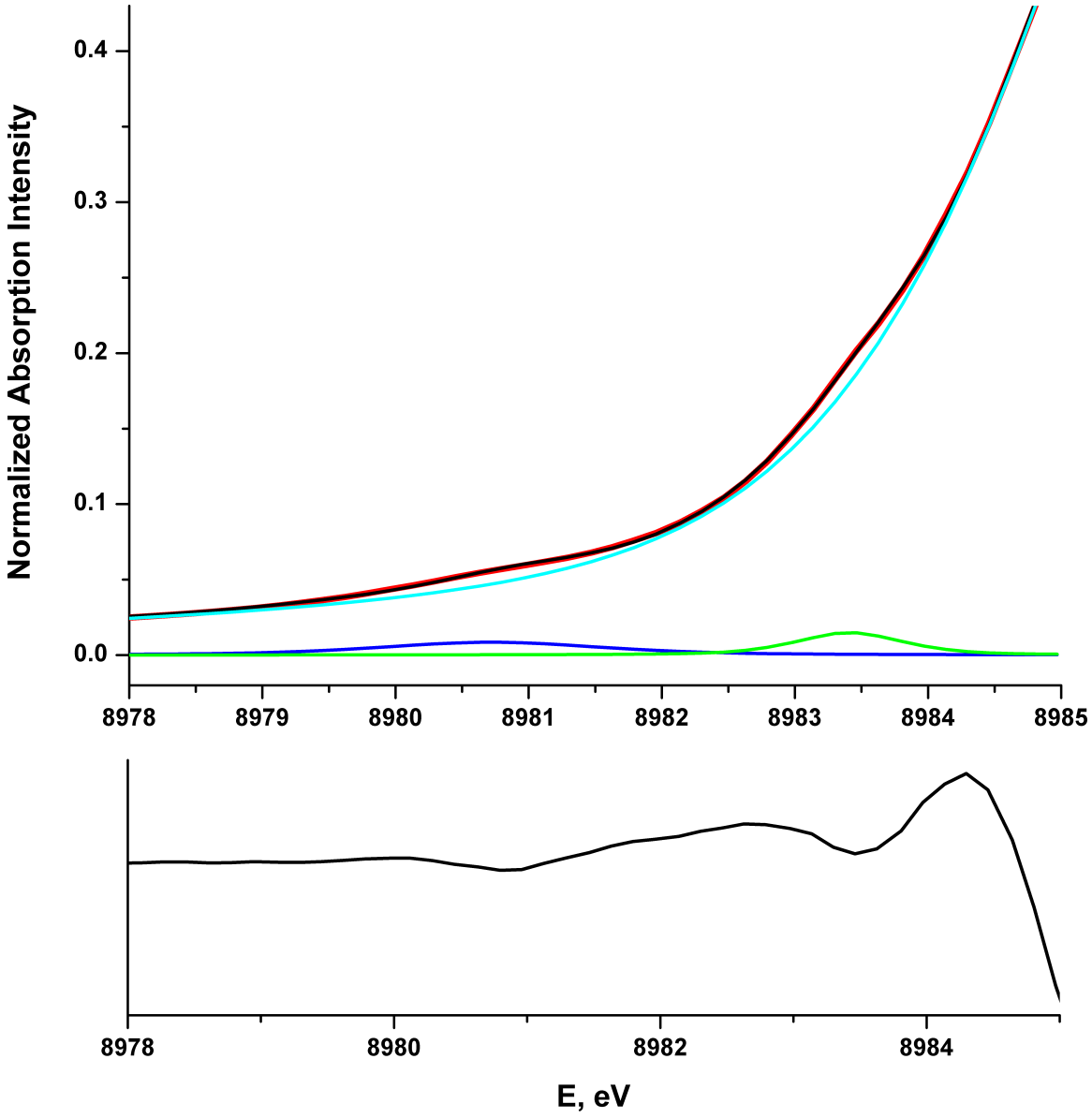


SI 4.4. Results of the fits to the initial pre-edge transition for **2**.

	Fit range / eV	Peak position / eV	Hwhm / eV	Peak height / au	Peak area[a]	Scaled peak area[b]
	8976-8983	8980.78	0.985	0.00888	0.018	1.8
	8976-8984	8980.85	1.07	0.00883	0.019	1.9
	8976-8985	8980.84	1.10	0.00916	0.020	2.0
Average		8980.82	1.05	0.00896	0.019	1.9
Standard deviation		0.04	0.06	0.00018	0.0013	0.13

[a] Peak area determined by multiplying the full-width at half-height by the peak height.
[b] Scaled peak area is equal to the peak area multiplied by 100.

SI 4.5. Representative fit to the experimental spectrum (top; experimental in black; components of the fit in blue, green, and cyan; sum of the fit in red) and 2nd derivative of the experimental spectrum (bottom) for complex **3**.

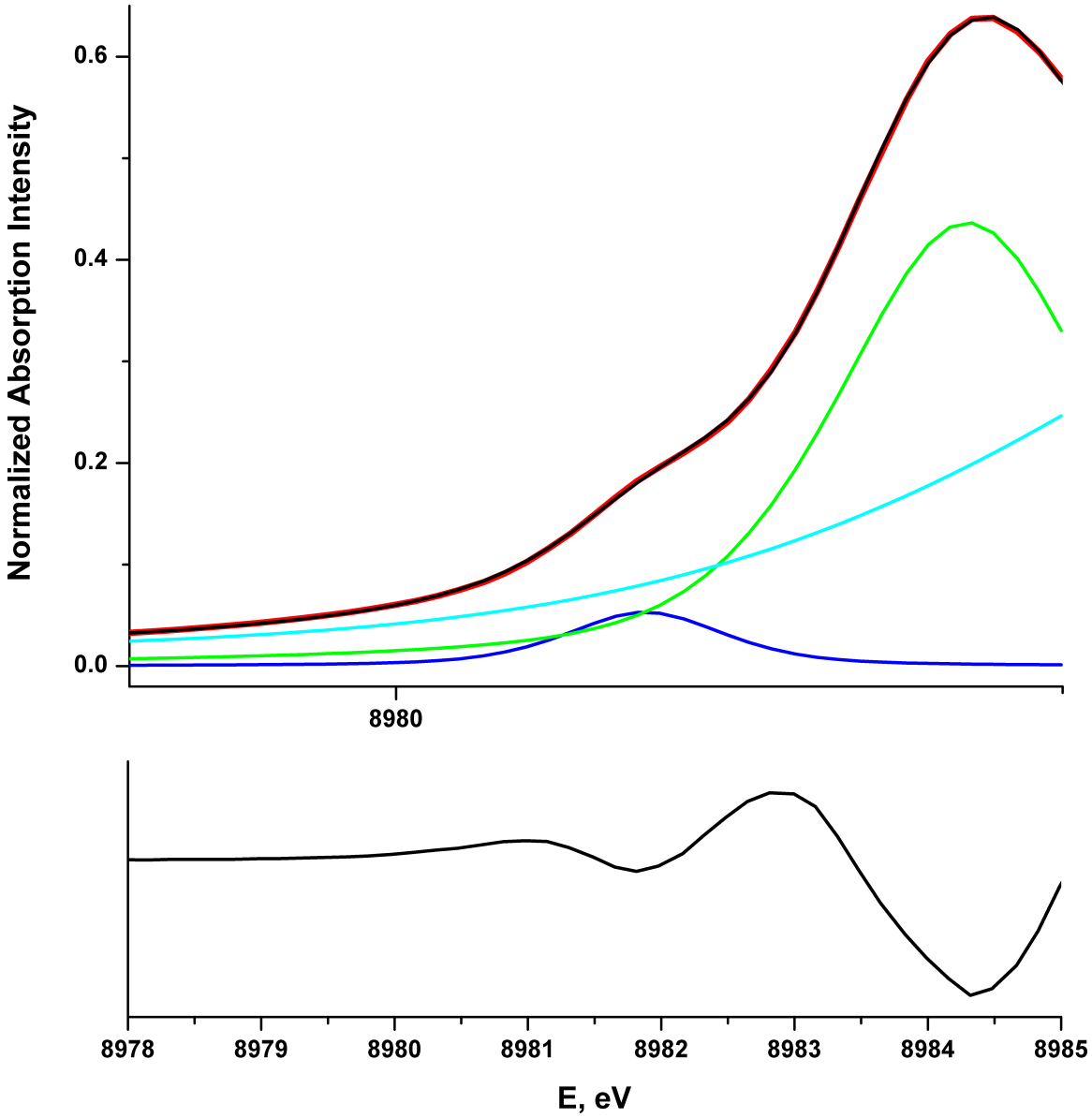


SI 4.6. Results of the fits to the initial pre-edge transition for **3**.

	Fit range / eV	Peak position / eV	Hwhm / eV	Peak height / au	Peak area[a]	Scaled peak area[b]
	8976-8983	8980.74	0.649	0.00625	0.0081	0.81
	8976-8984	8980.75	0.699	0.00722	0.010	1.0
	8976-8985	8980.72	0.999	0.00858	0.017	1.7
Average		8980.74	0.782	0.00735	0.012	1.2
Standard deviation		0.02	0.189	0.00117	0.0047	0.47

[a] Peak area determined by multiplying the full-width at half-height by the peak height.
[b] Scaled peak area is equal to the peak area multiplied by 100.

SI 4.7. Representative fit to the experimental spectrum (top; experimental in black; components of the fit in blue, green, and cyan; sum of the fit in red) and 2nd derivative of the experimental spectrum (bottom) for complex **4**.

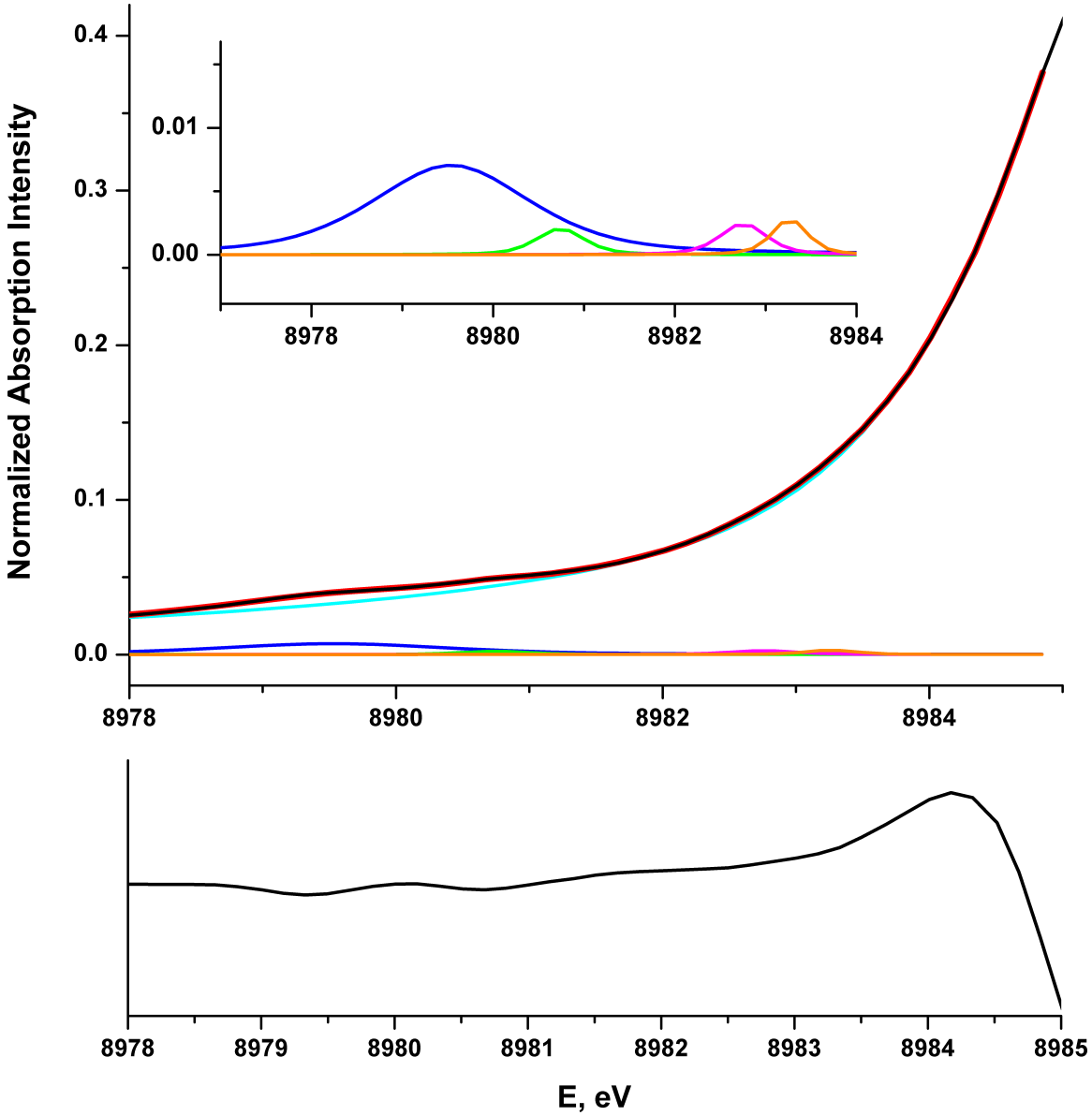


SI 4.8. Results of the fits to the initial pre-edge transition for **4**.

	Fit range / eV	Peak position / eV	Hwhm / eV	Peak height / au	Peak area[a]	Scaled peak area[b]
	8976-8983	8981.90	0.781	0.0566	0.088	8.8
	8976-8984	8981.87	0.711	0.0540	0.077	7.7
	8976-8985	8981.87	0.705	0.0532	0.075	7.5
Average		8981.88	0.732	0.0546	0.080	8.0
Standard deviation		0.02	0.042	0.0018	0.0072	0.72

[a] Peak area determined by multiplying the full-width at half-height by the peak height.
[b] Scaled peak area is equal to the peak area multiplied by 100.

SI 4.9. Representative fit to the experimental spectrum (top; experimental in black; components of the fit in blue, green, pink, orange, and cyan; sum of the fit in red) and 2nd derivative of the experimental spectrum (bottom) for complex **5**. The features at 8980.8 and 8983.2 eV result from contamination by **2**, the direct synthetic precursor to **5**.

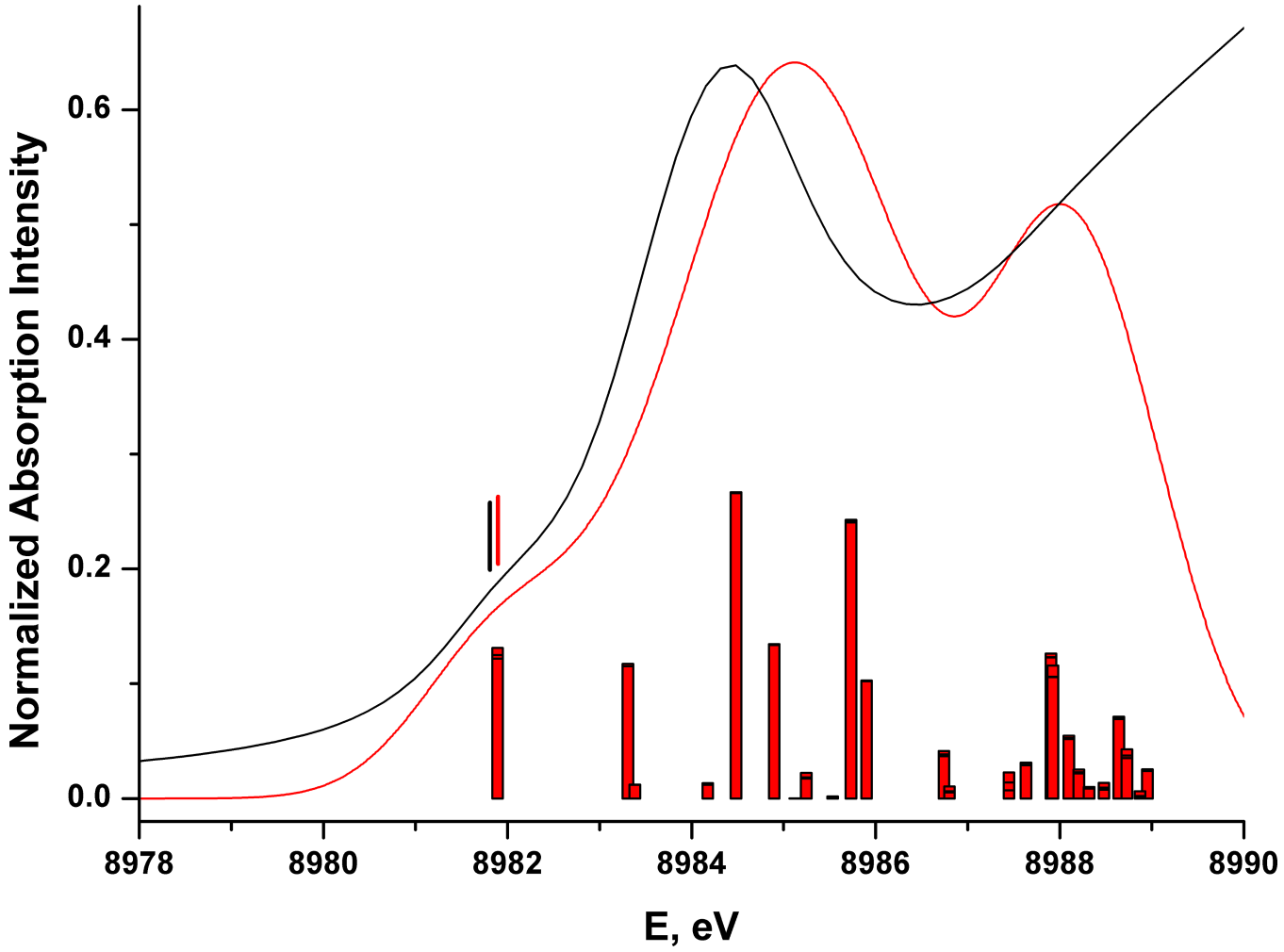


SI 4.10. Results of the fits to the initial pre-edge transition for **5**.

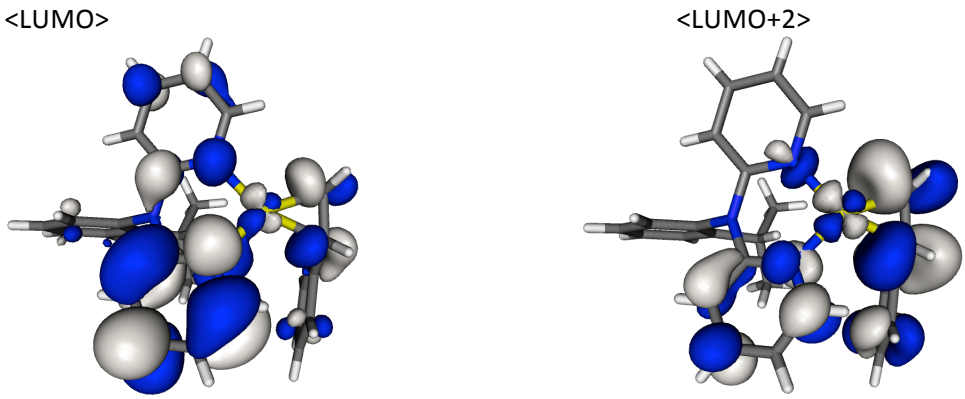
	Fit range / eV	Peak position / eV	Hwhm / eV	Peak height / au	Peak area[a]	Scaled peak area[b]
	8976-8983	8979.46	0.877	0.00732	0.013	1.3
	8976-8984	8979.46	0.896	0.00729	0.013	1.3
	8976-8985	8979.57	1.00	0.00664	0.013	1.3
Average		8979.50	0.925	0.00708	0.013	1.3
Standard deviation		0.06	0.066	0.00038	0.0003	0.03

[a] Peak area determined by multiplying the full-width at half-height by the peak height.
[b] Scaled peak area is equal to the peak area multiplied by 100.

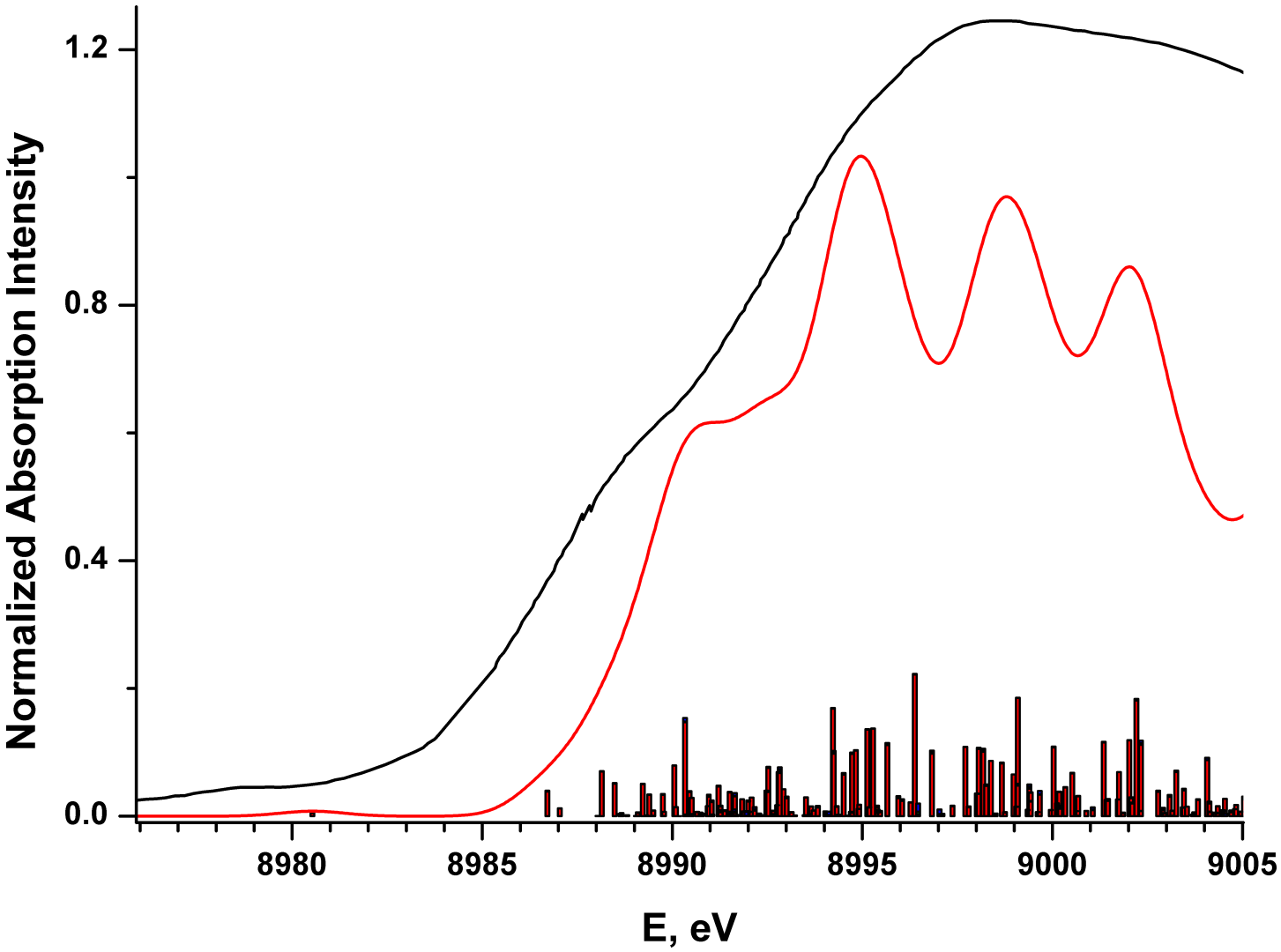
SI 5.1. Experimental Cu K-edge XAS spectrum of **4** (black) and calculated Cu K-edge XAS spectrum of $\mathbf{7}^{+}$ (red) with individual calculated transition energies (vertical bars). TD-DFT calculations on $\mathbf{7}^{+}$ were performed as described in the Experimental section, using the crystallographically determined molecular coordinates of the cation. The vertical black and red sticks above the solid traces illustrate the experimental (**4**) and calculated ($\mathbf{7}^{+}$) initial pre-edge transition energies.



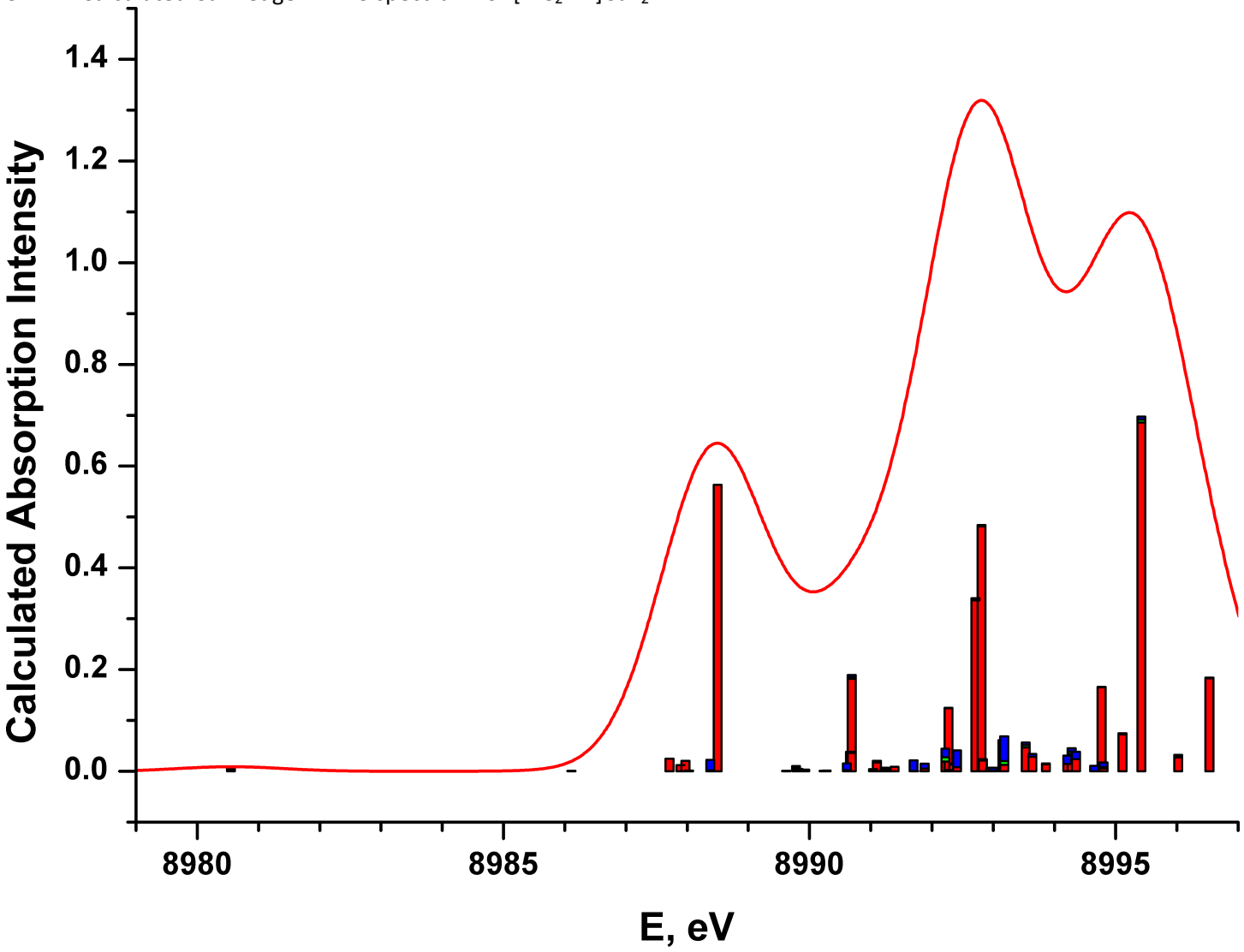
SI 5.2. The calculated transition at 8981.9 eV enters a state comprised of 23.8 % <LUMO> and 70.7 % <LUMO+2>.



SI 6. Comparison of experimental (black) and calculated (red) Cu K-edge XANES data for **6**. The experimental data were obtained from the literature.[26]

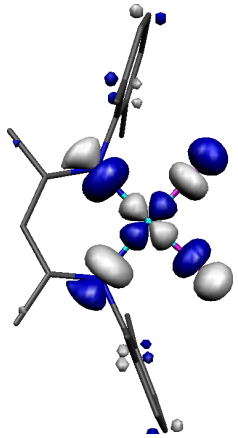


SI 7.1. Calculated Cu K-edge XANES spectrum for $[Me_2NN]CuF_2$.



SI 7.2. The calculated transitions at 8980.2 eV enters a state comprised of 99% <LUMO>.

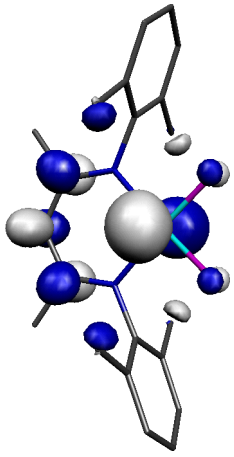
<LUMO>



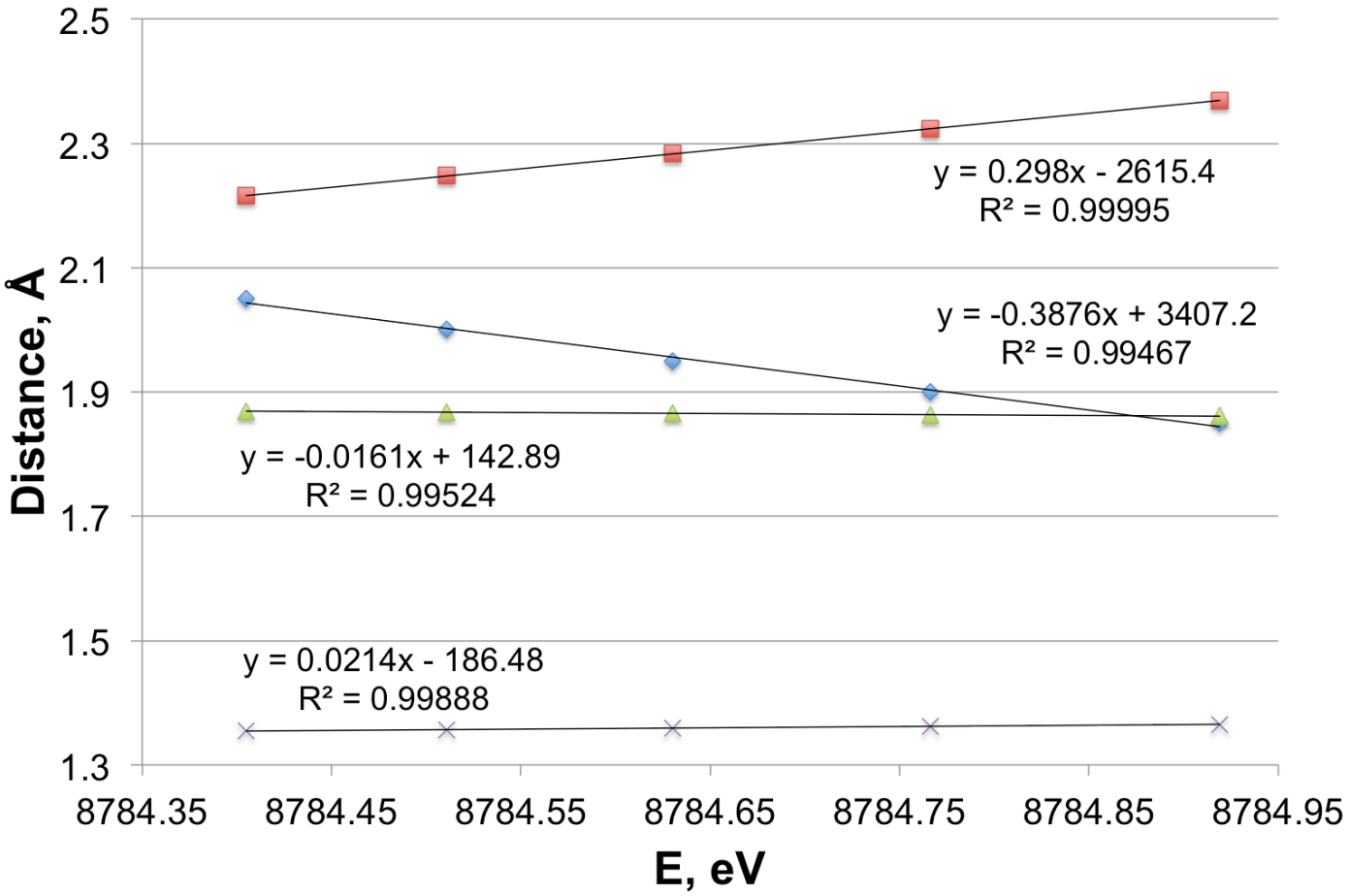
Fragment	% in LUMO
Cu-d_{xz}	40.4
F	21.7
[Me_2*NN*]	18.7

Fragment	% in LUMO+7
Cu-$4p_y$	39.8
F	3.6
[Me_2NN]	54.1

<LUMO+7>



SI 8.1. Results from a relaxed coordinate scan of the Cu–N_{eq} distance in TpCu(O_2), plotted against the calculated initial Cu pre-K-edge transition energy for each optimized geometry. The Cu–N_{eq} distance (blue diamonds) was constrained to values of 1.85, 1.90, 1.95, 2.00, and 2.05 Å as the geometry of the molecule was optimized (BP86, see experimental section). The resulting Cu–N_{ax} (red squares), Cu–O (green triangles), and O–O (grey crosses) distances are plotted, along with the associated linear fit to each data series.



SI 8.2. Tabulated results from the relaxed coordinate scan of the Cu–N_{eq} bonds and subsequent calculation of the initial Cu pre-K-edge transition energy.

Cu–N_{eq} / Å	Cu-N_{ax} / Å	Cu–O / Å	O–O / Å	LUMO		Pre-edge / eV
				% d_{xz}	% O-p_z	
1.8500	2.3689	1.8614	1.3654	31.0	46.8	8784.919
1.9000	2.3236	1.8635	1.3624	30.9	47.6	8784.766
1.9500	2.2836	1.8656	1.3595	30.6	48.4	8784.630
2.0000	2.2479	1.8676	1.3569	30.3	48.8	8784.511
2.0500	2.2155	1.8697	1.3544	29.8	49.0	8784.405

SI 9. Comparison of DFT and multiconfiguration ab initio methods.

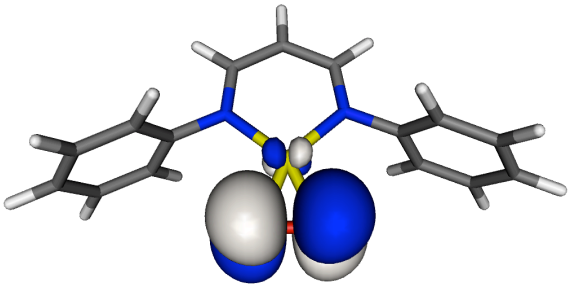
Analysis of the ground state electronic structures of complexes **1**-**4** and **6** highlight the difficulty in evaluating multi-determinant systems with ligand field and density functional theories. The broken symmetry (BS) methodology originally developed by Noodleman *et al.*[27,28] has traditionally performed well at modeling the multi-determinantal nature of a range of complexes with DFT, but the *S* = 0 species **1**-**4** failed to yield BS solutions, despite presenting clear multi-determinant ground states by *ab initio* methods.

Related studies have addressed the limitations of most single-determinate methods when describing multi-determinate states, but the popularity of the BS methodology begs a comment on why this methodology failed for most of the complexes studied herein. The BS methodology as applied to multi-determinant singlets often relies on two common factors: *i*) a close energetic proximity between the ground state and the lowest energy $^1A_1$ excited state and *ii*) the representation of these two states by the determinants $^1\Phi_0 = |(\phi_A + \phi_B)^2(\phi_A - \phi_B)^0>$ and $^1\Phi_3 = |(\phi_A + \phi_B)^0(\phi_A - \phi_B)^2>$, where $\phi_{A(B)}$ refers to a fragment orbital originating from A(B). In a simplified sense, the BS methodology uses the lowest energy triplet state to generate an approximation of the orbital character of $^1\Phi_3$. Thus, if the singlet and triplet states derived by DFT are comprised of orbitals that do not represent bonding and anti-bonding combinations of ϕ_A and ϕ_B (or, more generally, do not have the appropriate symmetry to mix), the BS methodology will not be able to generate the localized orbitals needed for separate representation of the α- and β-electrons in the single determinant available within DFT. Using **1** as an example, $^1\Phi_0$ is of A_1 symmetry and can be described as $(1b_2)^2(1a_2)^2(2b_2)^0$, but DFT and *ab initio* computation methods both predict $^3\Phi_0$ for this species to be $(1b_2)^2(1a_2)^1(2b_2)^1$, a B_1 configuration, not the A_1-symmetric $(1b_2)^1(1a_2)^2(2b_2)^1$ as would be required for mixing with $^1\Phi_0$. Thus, the BS methodology fails in these cases because the lowest energy triplet state is of a different character than the A_1 ground state.

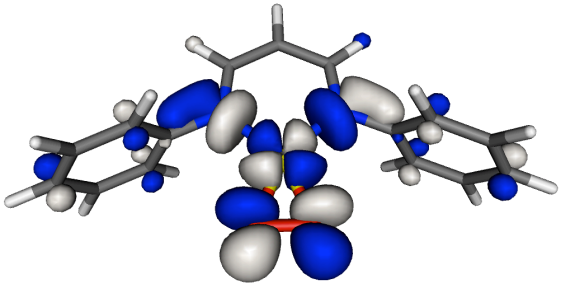
SI 10. Broken symmetry (1,1) B3LYP/def2-TZVP, def2-TZV/J (Cu,N,O)/def2-SV(P), def2-SV/J single point energy calculation on **1'**.

Final single-point energy: -2478.898086161746 E_h (+5.0 kcal/mol vs. RKS solution)
J = 1218.93 cm^{-1} (from $J = -(E_{HS}-E_{BS})/(<S^2>_{HS}-<S^2>_{BS})$)[29,30]
$S_{\alpha\beta}$(HOMO): 0.005

<HOMO-α>



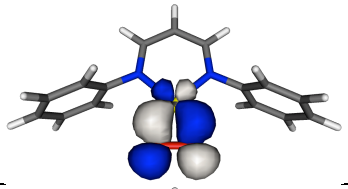
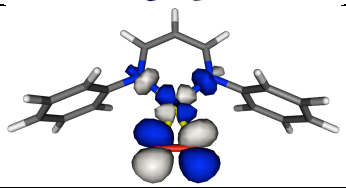
<HOMO-β>



SI 11.1. CASSCF computational results: CAS(2,2) S = 0 (v = 0)

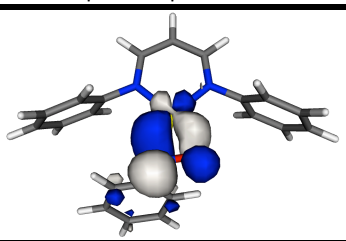
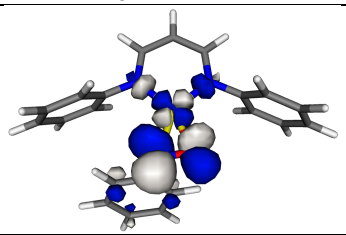
1': E = -2472.6940598883 E_h

Configuration no.	Configuration weight	Representative electron configurations	
		<80>	<81>
1	0.82084	↑↓	
2	0.17916		↑↓

Orbital no.	Graphical representation	Orbital description	Occupation
80		$<d_{xz} + \pi^*_{ip}>$	1.641683
81		$<d_{xz} - \pi^*_{ip}>$	0.358317

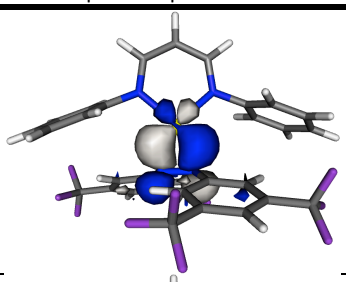
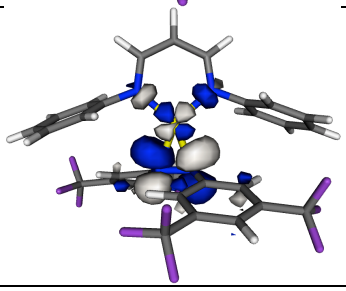
2': E = -2682.2671563581 E_h

Configuration no.	Configuration weight	Representative electron configurations	
		<100>	<101>
1	0.79840	↑↓	
2	0.20160		↑↓

Orbital no.	Graphical representation	Orbital description	Occupation
100		$<d_{xz} + \pi^*_{ip}>$	1.596793
101		$<d_{xz} - \pi^*_{ip}>$	0.403207

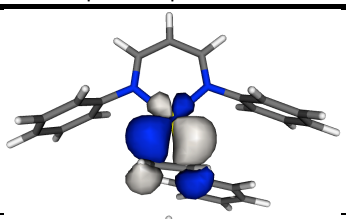
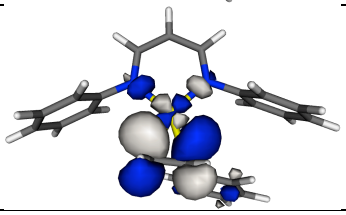
3': E = -4233.1912361990 E_h

Configuration no.	Configuration weight	Representative electron configurations	
		<184>	<185>
1	0.82694	↑↓	
2	0.17306		↑↓

Orbital no.	Graphical representation	Orbital description	Occupation
184		$<d_{xz} + \pi^*_{ip}>$	1.653871
185		$<d_{xz} - \pi^*_{ip}>$	0.346129

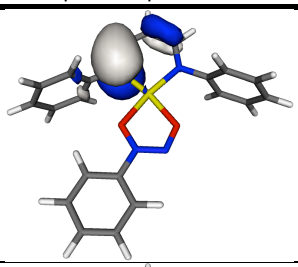
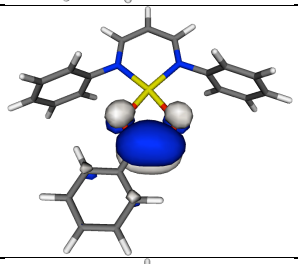
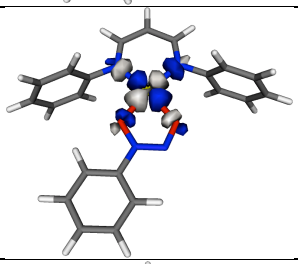
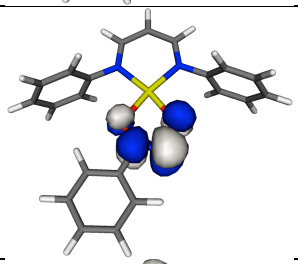
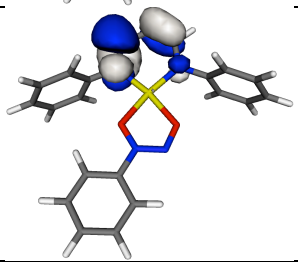
4': E = -2630.4389283856 E_h

Configuration no.	Configuration weight	Representative electron configurations	
		<100>	<101>
1	0.91824	↑↓	
2	0.08176		↑↓

Orbital no.	Graphical representation	Orbital description	Occupation
100		$<d_{xz} + \pi^*_{ip}>$	1.836478
101		$<d_{xz} - \pi^*_{ip}>$	0.163522

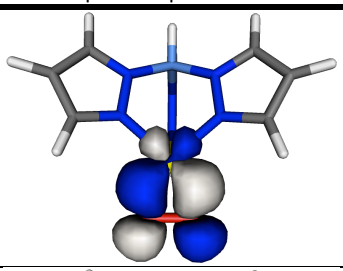
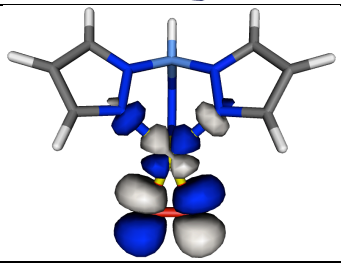
5', CAS(5,5): E = -2811.6389037615 E_h

Configuration no.	Configuration weight	Representative electron configurations				
		<106>	<107>	<108>	<109>	<110>
1	0.92413	↑↓	↑↓	↑		
2	0.05169	↑↓		↑	↑↓	
3	0.02283		↑↓	↑		↑↓

Orbital no.	Graphical representation	Orbital description	Occupation
106		[Me2NN]-π	1.951719
107		PhN_2O_2-π	1.894016
108		d_{xz}	0.999999
109		PhN_2O_2-π	0.105966
110		[Me2NN]-π	0.048300

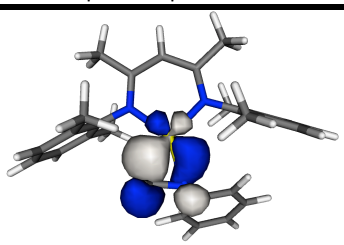
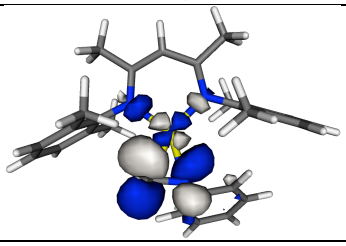
6': E = -2486.5112633846 E_h

Configuration no.	Configuration weight	Representative electron configurations	
		<77>	<78>
1	0.80364	↑↓	
2	0.19636		↑↓

Orbital no.	Graphical representation	Orbital description	Occupation
77		$<d_{xz} + \pi^*_{ip}>$	1.607272
78		$<d_{xz} - \pi^*_{ip}>$	0.392728

8: E = -2880.4591088750 E_h

Configuration no.	Configuration weight	Representative electron configurations	
		<124>	<125>
1	0.88347	↑↓	
2	0.11653		↑↓

Orbital no.	Graphical representation	Orbital description	Occupation
124		$<d_{xz} + \pi^*_{ip}>$	1.766937
125		$<d_{xz} - \pi^*_{ip}>$	0.233063

SI 11.2. CASSCF computational results: SA-CAS(4,3) S = 0 (v = 0) and S = 0 (v' = 0)

1': Root 0: E= -2472.6904501526 E_h
Root 1: E= -2472.6690752761 E_h
SA-CASSCF transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
0:	1	1	4691.2

Root no.	Configuration no.	Configuration weight	Representative electron configurations			
			<79>	<80>	<81>	
0	1	0.65632	↑↓	↑↓		
0	2	0.22490	↑	↑↓	↓	
0	3	0.11867		↑↓	↑↓	
1	1	0.89047	↑↓	↑	↓	
1	2	0.10953	↑	↓	↑↓	
			<d_{xz} + π*$_{ip}$>	<π*$_{oop}$>	<d_{xz} – π*$_{ip}$>	Orbital description
			1.714121	1.499887	0.785992	Occupation

2': Root 0: E = -2682.2581645616 E_h
Root 1: E = -2682.1811487183 E_h
SA-CASSCF transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
0:	1	1	16903.0

Root no.	Configuration no.	Configuration weight	Representative electron configurations			
			<99>	<100>	<101>	
0	1	0.58210	↑↓	↑↓		
0	2	0.21597	↑	↑↓	↓	
0	3	0.10746		↑↓	↑↓	
0	4	0.08374	↑↓	↑	↓	
0	5	0.01064	↑	↓	↑↓	
1	1	0.80437	↑↓	↑	↓	
1	2	0.10124	↑	↓	↑↓	
1	3	0.06056	↑↓	↑↓		
1	4	0.02226	↑	↑↓	↓	
1	5	0.01156		↑↓	↑↓	
			<d_{xz} + π*$_{ip}$>	<π*$_{oop}$>	<d_{xz} – π*$_{ip}$>	Orbital description
			1.705927	1.499899	0.794174	Occupation

3': Root 0: E = -4233.1860699016 E_h
Root 1: E = -4233.0797448536 E_h
SA-CASSCF transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
0:	1	1	23335.7

Root no.	Configuration no.	Configuration weight	Representative electron configurations			
			<183>	<184>	<185>	
0	1	0.64011	↑↓	↑↓		
0	2	0.24263	↑	↑↓	↓	
0	3	0.11713		↑↓	↑↓	
1	1	0.88501	↑↓	↑	↓	
1	2	0.11493	↑	↓	↑↓	
			<d_{xz} + π*$_{ip}$>	<π*$_{oop}$>	<d_{xz} – π*$_{ip}$>	Orbital description
			1.714121	1.499887	0.785992	Occupation

6': Root 0: E = -2486.5076647107 E_h
Root 1: E = -2486.4920497222 E_h
SA-CASSCF transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
0:	1	1	3427.1

Root no.	Configuration no.	Configuration weight	Representative electron configurations			
			<76>	<77>	<78>	
0	1	0.62185	↑↓	↑↓		
0	2	0.25367	↑	↑↓	↓	
0	3	0.12393		↑↓	↑↓	
1	1	0.89106	↑↓	↑	↓	
1	2	0.10851	↑	↓	↑↓	
			<d_{xz} + π*$_{ip}$>	<π*$_{oop}$>	<d_{xz} – π*$_{ip}$>	Orbital description
			1.694851	1.499885	0.805264	Occupation

SI 11.3. CASSCF computational results: SA-CAS(4,3) S = 0 (v = 0) and S = 1 (v = 0)

1': State 0: E = -2472.6905814538 E_h
State 1: E = -2472.6725365328 E_h
SA-CASSCF transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
1:	0	3	3960.4

State	Configuration no.	Configuration weight	Representative electron configurations			
			<79>	<80>	<81>	
S = 0 (v = 0)	1	0.66600	↑↓	↑↓		
S = 0 (v = 0)	2	0.21202	↑	↑↓	↓	
S = 0 (v = 0)	3	0.12186		↑↓	↑↓	
S = 1 (v = 0)	1	0.89689	↑↓	↑	↑	
S = 1 (v = 0)	2	0.10311	↑	↑	↑↓	
			<d_{xz} + π*$_{ip}$>	<π*$_{oop}$>	<d_{xz} – π*$_{ip}$>	Orbital description
			1.720571	1.499882	0.779547	Occupation

2': State 0: E = -2682.2647605964 E_h
State 1: E = -2682.2279283320 E_h
SA-CASSCF transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
1:	0	3	8083.7

State	Configuration no.	Configuration weight	Representative electron configurations			
			<99>	<100>	<101>	
S = 0 (v = 0)	1	0.76831	↑↓	↑↓		
S = 0 (v = 0)	2	0.21851	↑↓		↑↓	
S = 1 (v = 0)	1	0.98918	↑↓	↑	↑	
			<π*$_{oop}$>	<d_{xz} + π*$_{ip}$>	<d_{xz} – π*$_{ip}$>	Orbital description
			1.98810	1.27931	0.73258	Occupation

3': State 0: E = -4233.1875648976 E_h
State 1: E = -4233.1377818188 E_h
SA-CASSCF transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
1:	0	3	10926.1

State	Configuration no.	Configuration weight	Representative electron configurations			
			<183>	<184>	<185>	
S = 0 (v = 0)	1	0.79557	↑↓	↑↓		
S = 0 (v = 0)	2	0.20439	↑↓		↑↓	
S = 1 (v = 0)	1	1.00000	↑↓	↑	↑	
			<π^*_{oop}>	<$d_{xz} + \pi^*_{ip}$>	<$d_{xz} - \pi^*_{ip}$>	Orbital description
			1.999956	1.295614	0.704431	Occupation

6': State 0: E = -2486.5078007276 E_h
State 1: E = -2486.4952522370 E_h
SA-CASSCF transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
1:	0	3	2754.1

State	Configuration no.	Configuration weight	Representative electron configurations			
			<76>	<77>	<78>	
S = 0 (v = 0)	1	0.63284	↑↓	↑↓		
S = 0 (v = 0)	2	0.23708	↑	↑↓	↓	
S = 0 (v = 0)	3	0.12425		↑↓	↑↓	
S = 1 (v = 0)	1	0.89466	↑↓	↑	↑	
S = 1 (v = 0)	2	0.10224	↑	↑	↑↓	
			<$d_{xz} + \pi^*_{ip}$>	<π^*_{oop}>	<$d_{xz} - \pi^*_{ip}$>	Orbital description
			1.702680	1.498509	0.798811	Occupation

SI 12.1. MR-DDCI3 computational results: CAS(2,2)/MR-DDCI3 S = 0 (v = 0), $T_{sel} = 10^{-8}$

1': E = -2472.971717602 E_h, Reference Weight = 0.9178

Configuration no.	Configuration weight	Representative electron configurations		
		<80>	<81>	
1	0.8351	↑↓		
2	0.0827		↑↓	
		$<d_{xz} + \pi^*_{ip}>$	$<d_{xz} - \pi^*_{ip}>$	Orbital description

2': E = -2682.527738908 E_h, Reference Weight = 0.9183

Configuration no.	Configuration weight	Representative electron configurations		
		<100>	<101>	
1	0.8330	↑↓		
2	0.0854		↑↓	
		$<d_{xz} + \pi^*_{ip}>$	$<d_{xz} - \pi^*_{ip}>$	Orbital description

3': E = -4233.462458827 E_h, Reference Weight = 0.9168

Configuration no.	Configuration weight	Representative electron configurations		
		<184>	<185>	
1	0.8535	↑↓		
2	0.0633		↑↓	
		$<d_{xz} + \pi^*_{ip}>$	$<d_{xz} - \pi^*_{ip}>$	Orbital description

4': E = -2630.677853273 E_h, Reference Weight = 0.9227

Configuration no.	Configuration weight	Representative electron configurations		
		<100>	<101>	
1	0.8987	↑↓		
2	0.0239		↑↓	
		$<d_{xz} + \pi^*_{ip}>$	$<d_{xz} - \pi^*_{ip}>$	Orbital description

5', CAS(5,5), $T_{sel} = 10^{-7}$, E = -2812.148017566 E_h, Reference Weight = 0.8821

Configuration no.	Configuration weight	Representative electron configurations					
		<106>	<107>	<108>	<109>	<110>	
1	0.8610	↑↓	↑↓	↑			
2	0.0142	↑↓		↑	↑↓		
3	0.0067		↑↓	↑		↑↓	
		<[Me2NN] – π>	<PhN_2O_2 – π>	$<d_{xz}>$	<PhN_2O_2 – π>	<[Me2NN] – π>	Orbital description

6', $T_{sel} = 10^{-7}$, E = -2486.777499028 E_h, Reference Weight = 0.9171

Configuration no.	Configuration weight	Representative electron configurations		
		<77>	<78>	
1	0.8343	↑↓		
2	0.0828		↑↓	
		$<d_{xz} + \pi^*_{ip}>$	$<d_{xz} - \pi^*_{ip}>$	Orbital description

8', $T_{sel} = 10^{-7}$, E = -2880.720082425 E_h, Reference Weight = 0.9091

Configuration no.	Configuration weight	Representative electron configurations		
		<124>	<125>	
1	0.8873	↑↓		
2	0.0219		↑↓	
3	0.0179	↑	↓	
		$<d_{xz} + \pi^*_{ip}>$	$<d_{xz} - \pi^*_{ip}>$	Orbital description

SI 12.2. MR-DDCI3 computational results: SA-CAS(4,3)/MR-DDCI3 S = 0 (v = 0) and S = 0 (v' = 0), $T_{sel} = 10^{-6}$

1': State 0: E = -2473.092348272 E_h, Reference Weight = 0.9135
State 1: E = -2473.066589960 E_h, Reference Weight = 0.9117
SA-CASSCF/MR-DDCI3 transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
0:	1	1	5653.3

Root no.	Configuration no.	Configuration weight	Representative electron configurations			
			<79>	<80>	<81>	
0	1	0.0311		↑↓	↑↓	
0	2	0.2239	↑	↑↓	↓	
0	3	0.6584	↑↓	↑↓		
1	1	0.0227	↑	↓	↑↓	
1	2	0.8890	↑↓	↑	↓	
			$<d_{xz} + \pi^*_{ip}>$	$<\pi^*_{oop}>$	$<d_{xz} - \pi^*_{ip}>$	Orbital description

2': State 0: E = -2682.679666836 E_h, Reference Weight = 0.9243
State 1: E = -2682.597876967 E_h, Reference Weight = 0.9236
SA-CASSCF/MR-DDCI3 transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
0:	1	1	17950.8

Root no.	Configuration no.	Configuration weight	Representative electron configurations			
			<99>	<100>	<101>	
0	1	0.0128		↑↓	↑↓	
0	2	0.2666	↑	↑↓	↓	
0	3	0.0723	↑↓	↑	↓	
0	4	0.5722	↑↓	↑↓		
1	1	0.0087	↑	↓	↑↓	
1	2	0.0199	↑	↑↓	↓	
1	3	0.8417	↑↓	↑	↓	
1	4	0.0519	↑↓	↑↓		
			$<d_{xz} + \pi^*_{ip}>$	$<\pi^*_{oop}>$	$<d_{xz} - \pi^*_{ip}>$	Orbital description

3': State 0: E = -4233.623711110 E_h, Reference Weight = 0.9270
State 1: E = -4233.525219757 E_h, Reference Weight = 0.9166
SA-CASSCF/MR-DDCI3 transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
0:	1	1	21616.4

Root no.	Configuration no.	Configuration weight	Representative electron configurations			
			<183>	<184>	<185>	
0	1	0.6086	↑↓	↑↓		
0	2	0.3076	↑	↑↓	↓	
0	3	0.0108		↑↓	↑↓	
1	1	0.9061	↑↓	↑	↓	
1	2	0.0104	↑	↓	↑↓	
			$<d_{xz} + \pi^*_{ip}>$	$<\pi^*_{oop}>$	$<d_{xz} - \pi^*_{ip}>$	Orbital description

6': State 0: E = -2486.899229290 E_h, Reference Weight = 0.9210
State 1: E = -2486.878866416 E_h, Reference Weight = 0.9218
SA-CASSCF/MR-DDCI3 transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
0:	1	1	4469.1

Root no.	Configuration no.	Configuration weight	Representative electron configurations			
			<76>	<77>	<78>	
0	1	0.6178	↑↓	↑↓		
0	2	0.2743	↑	↑↓	↓	
0	3	0.0283		↑↓	↑↓	
1	1	0.9002	↑↓	↑	↓	
1	2	0.0212	↑	↓	↑↓	
			$<d_{xz} + \pi^*_{ip}>$	$<\pi^*_{oop}>$	$<d_{xz} - \pi^*_{ip}>$	Orbital description

SI 12.3. MR-DDCI3 computational results: SA-CAS(4,3)/MR-DDCI3 S = 0 (v = 0) and S = 1 (v = 0), $T_{sel} = 10^{-6}$

1': S = 0 (v = 0), STATE 0: E = -2473.092701833 E_h, Reference Weight = 0.9134
S = 1 (v = 0), STATE 0: E = -2473.080074370 E_h, Reference Weight = 0.9072
SA-CASSCF/MR-DDCI3 transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
1:	0	3	2771.4

State	Configuration no.	Configuration weight	Representative electron configurations			
			<79>	<80>	<81>	
S = 0 (v = 0)	1	0.6674	↑↓	↑↓		
S = 0 (v = 0)	2	0.2125	↑	↑↓	↓	
S = 0 (v = 0)	3	0.0333		↑↓	↑↓	
S = 1 (v = 0)	1	0.8961	↑↓	↑	↑	
S = 1 (v = 0)	2	0.0112	↑	↑	↑↓	
			$<d_{xz} + \pi^*_{ip}>$	$<\pi^*_{oop}>$	$<d_{xz} - \pi^*_{ip}>$	Orbital description

2': S = 0 (v = 0), STATE 0: E = -2682.664865507 E_h, Reference Weight = 0.9330
S = 1 (v = 0), STATE 0: E = -2682.614121830 E_h, Reference Weight = 0.9400
SA-CASSCF/MR-DDCI3 transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
1:	0	3	11136.9

State	Configuration no.	Configuration weight	Representative electron configurations			
			<99>	<100>	<101>	
S = 0 (v = 0)	1	0.8308	↑↓	↑↓		
S = 0 (v = 0)	2	0.0078	↑↓	↑	↓	
S = 0 (v = 0)	3	0.0750	↑↓		↑↓	
S = 0 (v = 0)	4	0.0183	↑	↑↓	↓	
S = 1 (v = 0)	1	0.9091	↑↓	↑	↑	
S = 1 (v = 0)	2	0.0306	↑	↑↓	↑	
			$<\pi^*_{oop}>$	$<d_{xz} + \pi^*_{ip}>$	$<d_{xz} - \pi^*_{ip}>$	Orbital description

3': S = 0 (v = 0), STATE 0: E = -4233.604200056 E_h, Reference Weight = 0.9332
S = 1 (v = 0), STATE 0: E = -4233.535888450 E_h, Reference Weight = 0.9396
SA-CASSCF/MR-DDCI3 transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
1:	0	3	14992.7

State	Configuration no.	Configuration weight	Representative electron configurations			
			<183>	<184>	<185>	
S = 0 (v = 0)	1	0.8593	↑↓	↑↓		
S = 0 (v = 0)	2	0.0739	↑↓		↑↓	
S = 1 (v = 0)	1	0.9396	↑↓	↑	↑	
			<π^*_{oop}>	<$d_{xz} + \pi^*_{ip}$>	<$d_{xz} - \pi^*_{ip}$>	Orbital description

6': S = 0 (v = 0), STATE 0: E = -2486.899442678 E_h, Reference Weight = 0.9224
S = 1 (v = 0), STATE 0: E = -2486.891222564 E_h, Reference Weight = 0.9172
SA-CASSCF/MR-DDCI3 transition energy:

STATE	ROOT	MULT	ΔE/cm^{-1}
0:	0	1	0.0
1:	0	3	1804.1

State	Configuration no.	Configuration weight	Representative electron configurations			
			<76>	<77>	<78>	
S = 0 (v = 0)	1	0.6375	↑↓	↑↓		
S = 0 (v = 0)	2	0.2535	↑	↑↓	↓	
S = 0 (v = 0)	3	0.0301		↑↓	↑↓	
S = 1 (v = 0)	1	0.9049	↑↓	↑	↑	
S = 1 (v = 0)	2	0.0104	↑	↑	↑↓	
			<$d_{xz} + \pi^*_{ip}$>	<π^*_{oop}>	<$d_{xz} - \pi^*_{ip}$>	Orbital description

SI 13.1. OVB analysis of CAS(2,2) wavefunctions.

1': E = -2472.6940598615 E_h

Configuration no.	Configuration weight	Representative electron configurations		Valence bond description	
		<80>	<81>		
1	0.87605	↑	↓	$Cu(II)/(O_2)^{\bullet 1-}$	
2	0.09140	↑↓		$Cu(I)/(O_2)^{0}$	
3	0.03255		↑↓	$Cu(III)/(O_2)^{2-}$	
		$<d_{xz}>$	$<\pi^*_{ip}>$		Orbital description

2': E = -2682.2671563621 E_h

Configuration no.	Configuration weight	Representative electron configurations		Valence bond description	
		<100>	<101>		
1	0.88525	↑	↓	$Cu(II)/(PhNO)^{\bullet 1-}$	
2	0.09708	↑↓		$Cu(I)/(PhNO)^{0}$	
3	0.01768		↑↓	$Cu(III)/(PhNO)^{2-}$	
		$<d_{xz}>$	$<\pi^*_{ip}>$		Orbital description

3': E = -4233.1912366010 E_h

Configuration no.	Configuration weight	Representative electron configurations		Valence bond description	
		<184>	<185>		
1	0.84833	↑	↓	$Cu(II)/(N_2Ar^F_2)^{\bullet 1-}$	
2	0.13623	↑↓		$Cu(I)/(N_2Ar^F_2)^{0}$	
3	0.01544		↑↓	$Cu(III)/(N_2Ar^F_2)^{2-}$	
		$<d_{xz}>$	$<\pi^*_{ip}>$		Orbital description

4': E = -2630.4389282910 E_h

Configuration no.	Configuration weight	Representative electron configurations		Valence bond description	
		<100>	<101>		
1	0.66525	↑	↓	$Cu(II)/(PhCHCH_2)^{\bullet 1-}$	
2	0.32415	↑↓		$Cu(I)/(PhCHCH_2)^{0}$	
3	0.01060		↑↓	$Cu(III)/(PhCHCH_2)^{2-}$	
		$<d_{xz}>$	$<\pi^*_{ip}>$		Orbital description

5': E = -2811.6389037920 E_h

Configuration no.	Configuration weight	Representative electron configurations					Valence bond description	
		<106>	<107>	<108>	<109>	<110>		
1	0.39944	↑	↑	↑	↓	↓	Cu(II)	
2	0.27201	↑	↑↓	↑	↓		Cu(II)	
3	0.12912	↑	↑		↑↓	↓	Cu(II)	
4	0.08614	↑	↑↓		↑↓		Cu(II)	
5	0.04058	↑	↑	↑↓		↓	Cu(II)	
6	0.03112	↑		↑	↓	↑↓	Cu(II)	
7	0.02820	↑	↑↓	↑↓			Cu(II)	
8	0.01027	↑			↑↓	↑↓	Cu(II)	
		$<d_{xz}>$	<[Me2NN]>	$<PhN_2O_2>$	$<PhN_2O_2>$	<[Me2NN]>		Orbital description

6': E = -2486.5112634198 E_h

Configuration no.	Configuration weight	Representative electron configurations		Valence bond description	
		<77>	<78>		
1	0.88855	↑	↓	$Cu(II)/(O_2)^{\bullet 1-}$	
2	0.08562	↑↓		$Cu(I)/(O_2)^{0}$	
3	0.02583		↑↓	$Cu(III)/(O_2)^{2-}$	
		$<d_{xz}>$	$<\pi^*_{ip}>$		Orbital description

8: E = -2880.4590358088 E_h

Configuration no.	Configuration weight	Representative electron configurations		Valence bond description	
		<124>	<125>		
1	0.75139	↑	↓	$Cu(II)/(PhNCH_2)^{\bullet 1-}$	
2	0.23590	↑↓		$Cu(I)/(PhNCH_2)^{0}$	
3	0.01271		↑↓	$Cu(III)/(PhNCH_2)^{2-}$	
		$<d_{xz}>$	$<\pi^*_{ip}>$		Orbital description

SI 13.2. OVB analysis of CAS(2,2)/MR-DDCI3 wavefunctions.

1': E = -2472.977043451 E_h, Reference Weight = 0.9176

Configuration no.	Configuration weight	Representative electron configurations		Valence bond description	
		<80>	<81>		
1	0.7023	↑	↓	$Cu(II)/(O_2)^{\bullet 1-}$	
2	0.1724	↑↓		$Cu(I)/(O_2)^{0}$	
3	0.0429		↑↓	$Cu(III)/(O_2)^{2-}$	
		$<d_{xz}>$	$<\pi^*_{ip}>$		Orbital description

2': E = -2682.542703466 E_h, Reference Weight = 0.9239

Configuration no.	Configuration weight	Representative electron configurations		Valence bond description	
		<100>	<101>		
1	0.6788	↑	↓	$Cu(II)/(PhNO)^{\bullet 1-}$	
2	0.2236	↑↓		$Cu(I)/(PhNO)^{0}$	
3	0.0215		↑↓	$Cu(III)/(PhNO)^{2-}$	
		$<d_{xz}>$	$<\pi^*_{ip}>$		Orbital description

3': E = -4233.486472952 E_h, Reference Weight = 0.9186

Configuration no.	Configuration weight	Representative electron configurations		Valence bond description	
		<184>	<185>		
1	0.6019	↑	↓	$Cu(II)/(N_2Ar^F_2)^{\bullet 1-}$	
2	0.2989	↑↓		$Cu(I)/(N_2Ar^F_2)^{0}$	
3	0.0178		↑↓	$Cu(III)/(N_2Ar^F_2)^{2-}$	
		$<d_{xz}>$	$<\pi^*_{ip}>$		Orbital description

4': E = -2630.697827275 E_h, Reference Weight = 0.9220

Configuration no.	Configuration weight	Representative electron configurations		Valence bond description	
		<100>	<101>		
1	0.4229	↑	↓	$Cu(II)/(PhCHCH_2)^{\bullet 1-}$	
2	0.4857	↑↓		$Cu(I)/(PhCHCH_2)^{0}$	
3	0.0134		↑↓	$Cu(III)/(PhCHCH_2)^{2-}$	
		$<d_{xz}>$	$<\pi^*_{ip}>$		Orbital description

5': E = -2812.172236747 E_h, Reference Weight = 0.8932

Configuration no.	Configuration weight	Representative electron configurations					Valence bond description	
		<106>	<107>	<108>	<109>	<110>		
1	0.3043	↑	↑	↑	↓	↓	Cu(II)	
2	0.2587	↑	↑↓	↑	↓		Cu(II)	
3	0.1219	↑	↑		↑↓	↓	Cu(II)	
4	0.1009	↑	↑↓		↑↓		Cu(II)	
5	0.0369	↑	↑	↑↓		↓	Cu(II)	
6	0.0257	↑		↑	↓	↑↓	Cu(II)	
7	0.0315	↑	↑↓	↑↓			Cu(II)	
8	0.0104	↑			↑↓	↑↓	Cu(II)	
		$<d_{xz}>$	<[Me2NN]>	$<PhN_2O_2>$	$<PhN_2O_2>$	<[Me2NN]>		Orbital description

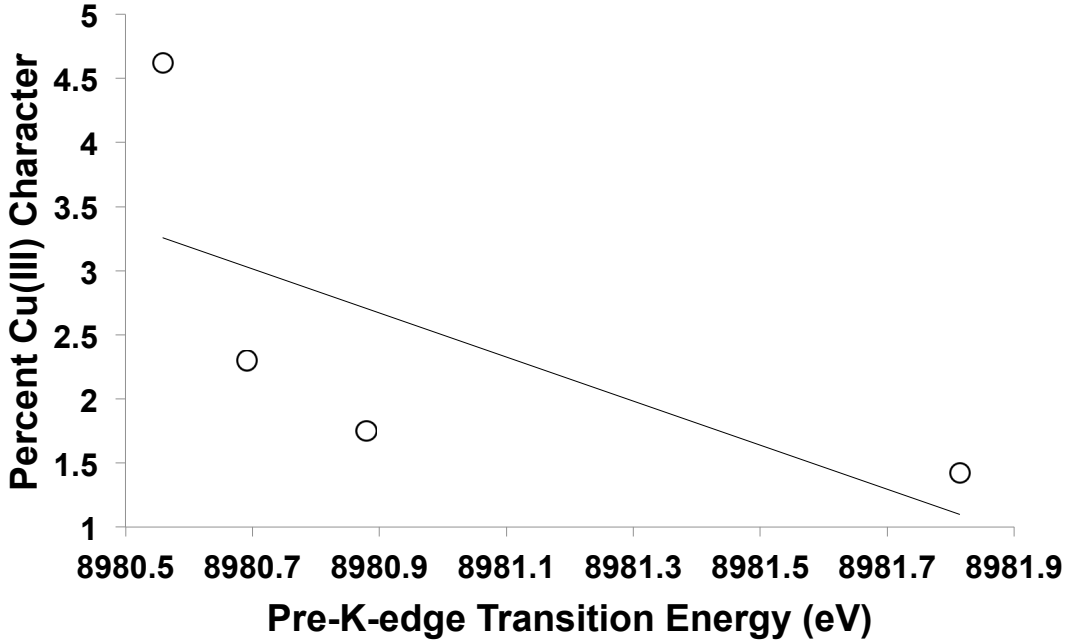
6': E = -2486.782006468 E_h, Reference Weight = 0.9192

Configuration no.	Configuration weight	Representative electron configurations		Valence bond description	
		<77>	<78>		
1	0.7177	↑	↓	$Cu(II)/(O_2)^{\bullet 1-}$	
2	0.1703	↑↓		$Cu(I)/(O_2)^{0}$	
3	0.0312		↑↓	$Cu(III)/(O_2)^{2-}$	
		$<d_{xz}>$	$<\pi^*_{ip}>$		Orbital description

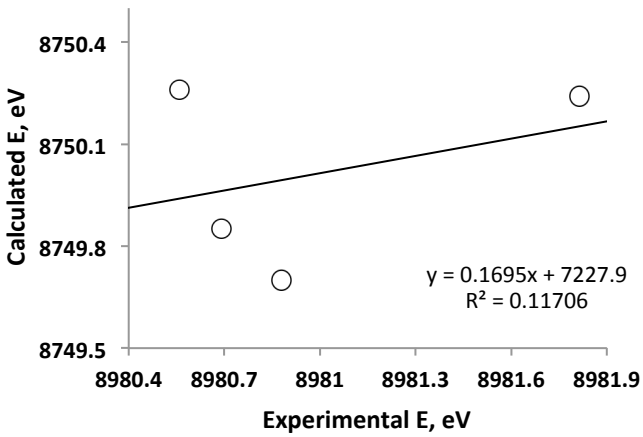
8: E = -2880.733054625 E_h, Reference Weight = 0.9224

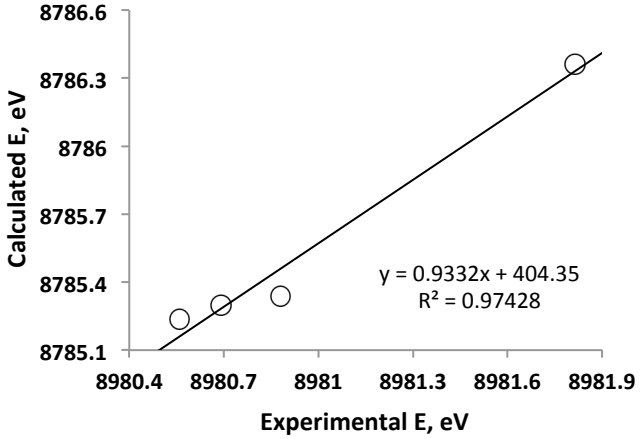
Configuration no.	Configuration weight	Representative electron configurations		Valence bond description	
		<124>	<125>		
1	0.4766	↑	↓	$Cu(II)/(PhNCH_2)^{\bullet 1-}$	
2	0.4317	↑↓		$Cu(I)/(PhNCH_2)^{0}$	
3	0.0141		↑↓	$Cu(III)/(PhNCH_2)^{2-}$	
		$<d_{xz}>$	$<\pi^*_{ip}>$		Orbital description

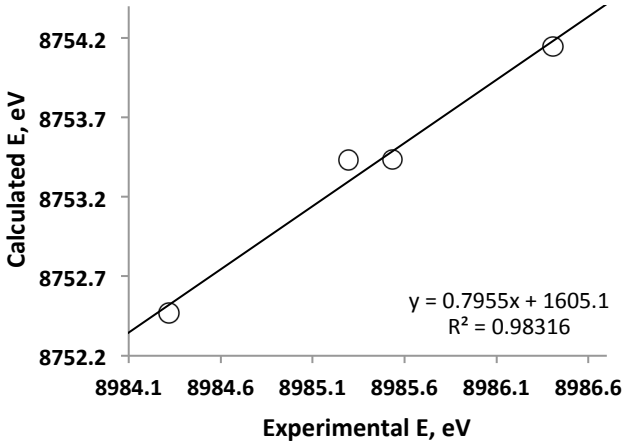
SI 14. Plot relating the experimental Cu pre-K-edge transition energy to the OVB-derived percent Cu(III) character in the molecular ground states of complexes **1**-**4**. The trendline was generated from the data points from complexes **1**-**4**: y = 15442 – 1.7191x; R^2 = 0.46.

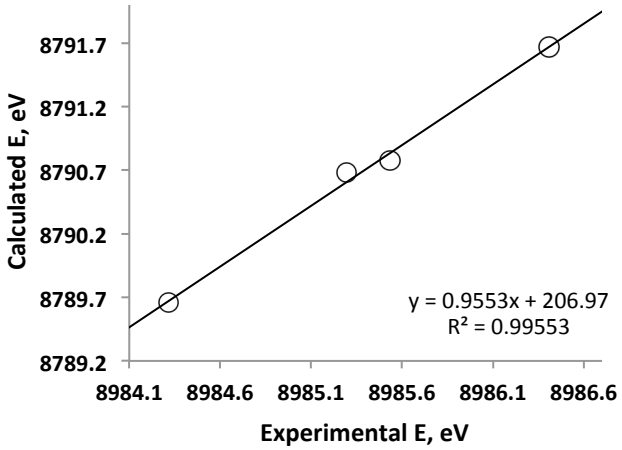


SI 15. Comparison of BP86 (left) and B3LYP (right) functionals for calculating pre-edge (top) and rising-edge (bottom) transition energies.

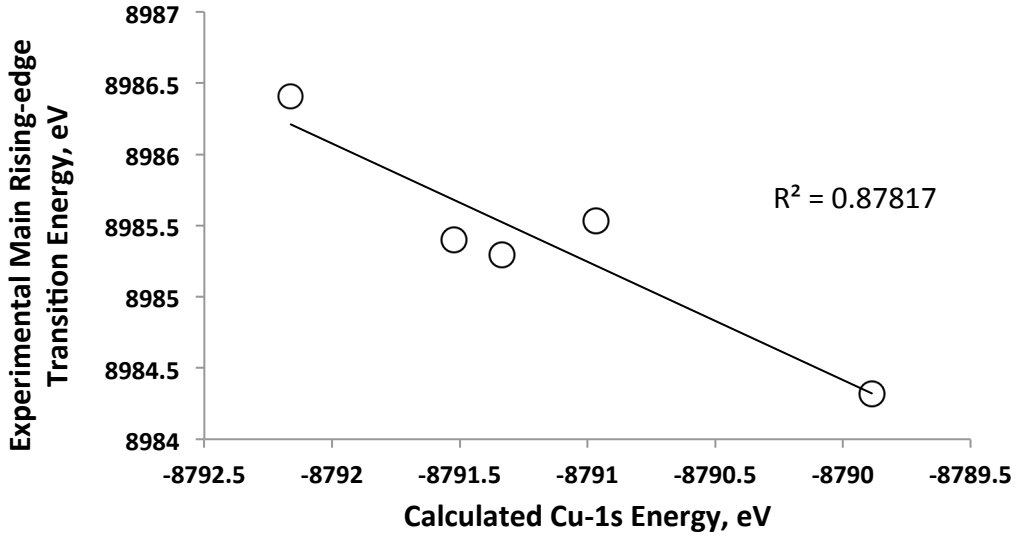


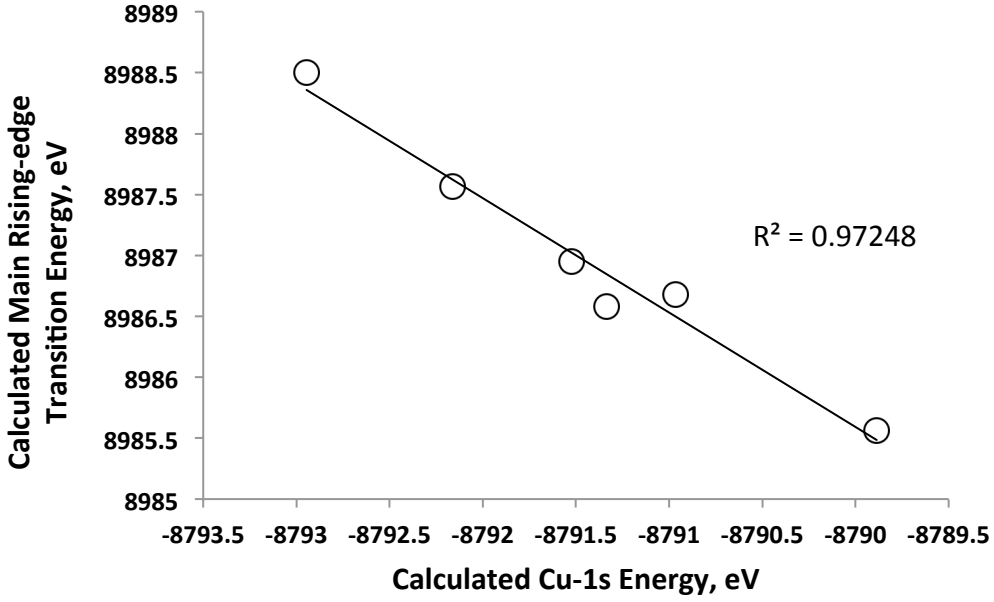




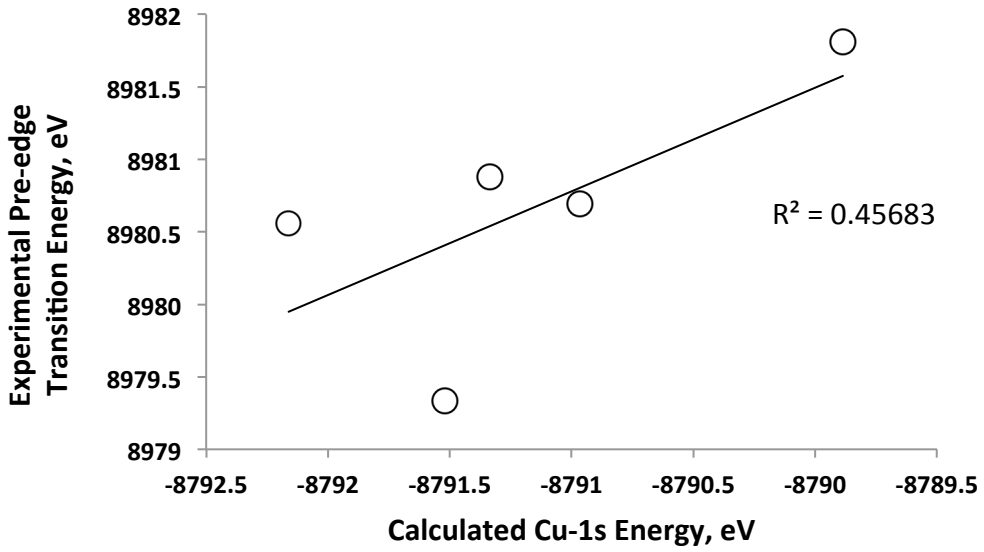


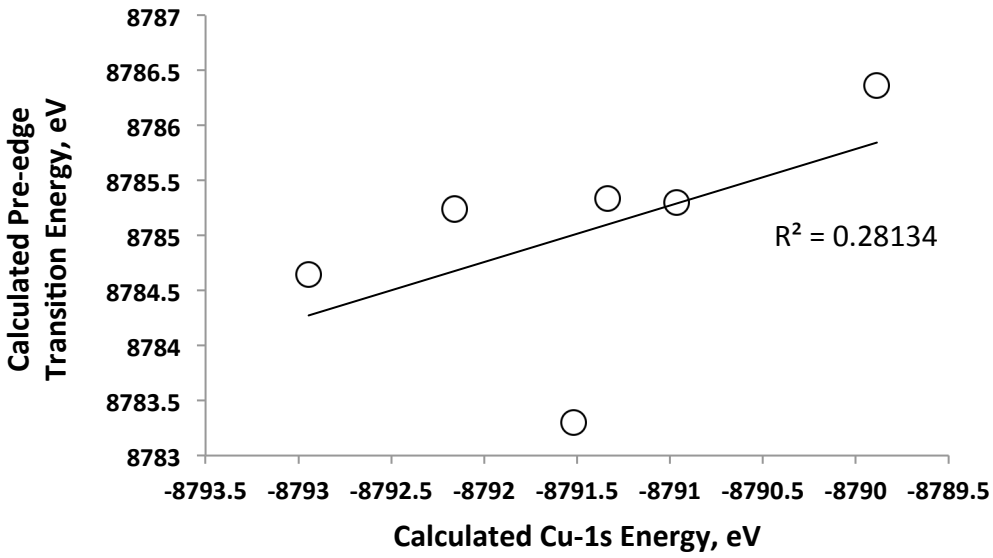
SI 16.1 Comparison of the calculated Cu-1s energies to the experimental (top) and calculated (bottom) main rising-edge transition for complexes **1**-**5** (top) and **1**-**5**, **9** (bottom).



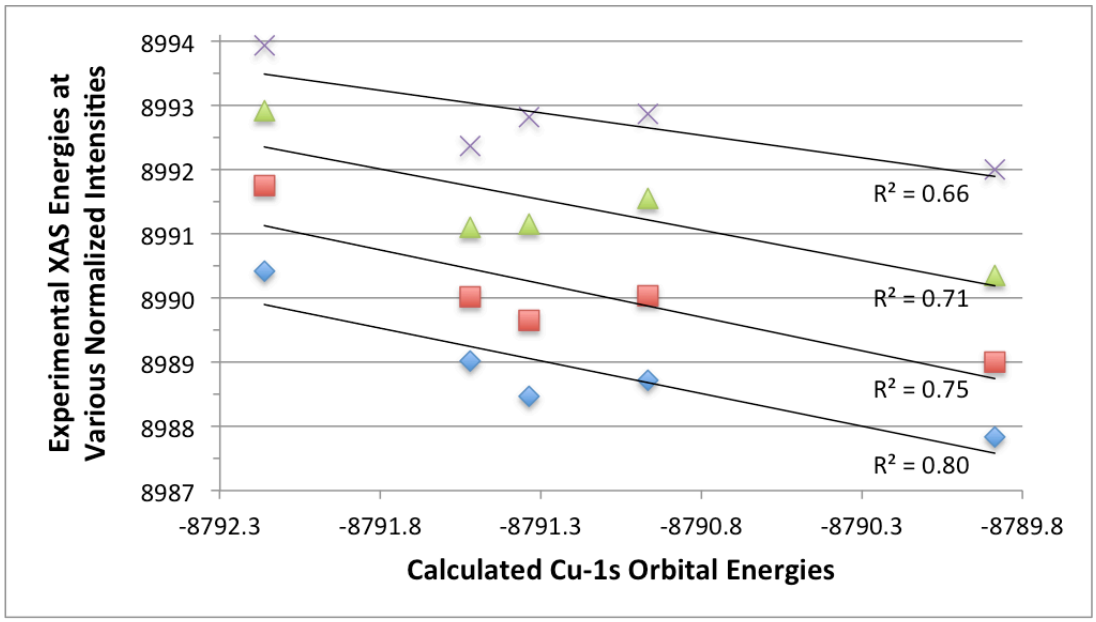


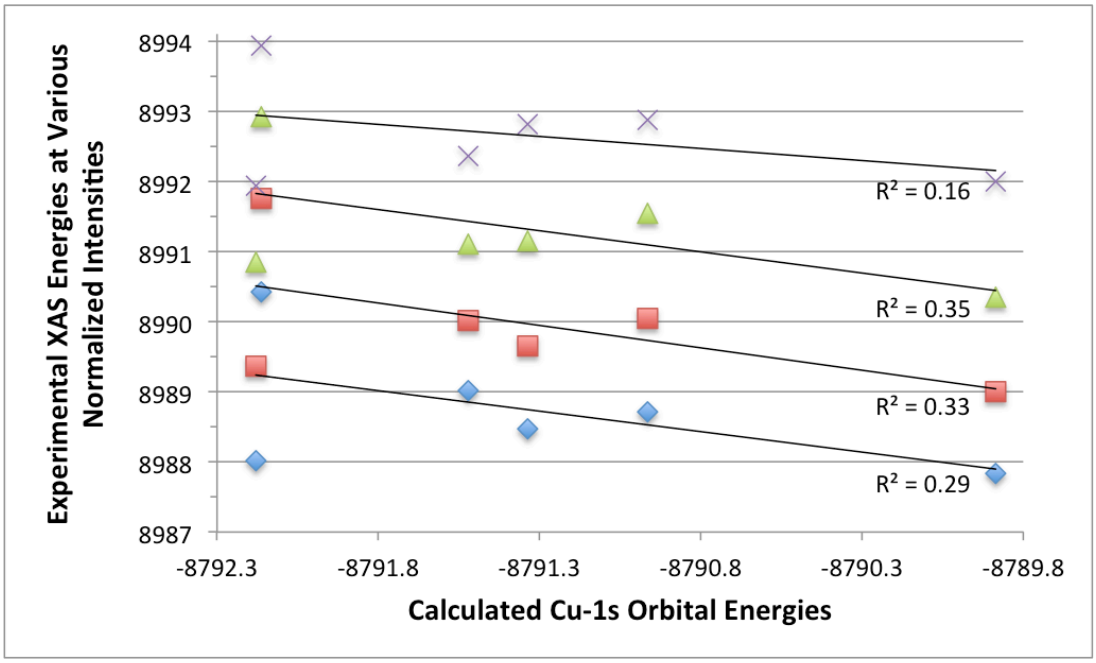
SI 16.2 Comparison of the calculated Cu-1s energies to the experimental (top) and calculated (bottom) pre-edge transition for complexes **1**-**5** (top) and **1**-**5**, **9** (bottom).





SI 17 Comparison of the calculated Cu-1s energies to the experimental XAS data at various normalized absorption intensities along the rising edge for compounds **1**-**5** (top) and **1**-**6** (bottom). Normalized absorption values of 0.5 (blue diamonds), 0.6 (red squares), 0.7 (green triangles), and 0.8 (grey crosses) are shown.





SI 18.1. Representative computational input for BP86 geometry optimization calculations. The def2-TZVP basis sets, along with the def2-TZV/J (**1**, **2**, **6**, **8**, and their truncated analogs) or def2-TZVP/J (**3**-**5** and their truncated analogs) auxiliary basis sets, were used for Cu and any atoms directly bound to the metal center.

```
! UKS BP86 RI SlowConv TightSCF def2-SV(P) def2-SV/J OPT NORMALPRINT

%basis NewGTO 29 "def2-TZVP" end
     NewGTO 8 "def2-TZVP" end
     NewGTO 7 "def2-TZVP" end
     NewAuxGTO 29 "def2-TZV/J"  end
     NewAuxGTO 8 "def2-TZV/J"  end
     NewAuxGTO 7 "def2-TZV/J"  end
     end

%scf directresetfreq 20
   diismaxeq 20
   MaxIter 700
   end

%geom  MaxIter 300
    end

*xyz 0 1
.
.
.
*
```

SI 18.2. Representative computational input for B3LYP single-point energy calculations. The def2-TZVP basis sets, along with the def2-TZV/J (**1**, **2**, **6**, **8**, and their truncated analogs) or def2-TZVP/J (**3**-**5** and their truncated analogs) auxiliary basis sets, were used for all atoms directly bound to the metal center. Either the def2-TZVP or CP(PPP) basis sets, along with the def2-TZV/J (**1**, **2**, **6**, **8**, and their truncated analogs) or def2-TZVP/J (**3**-**5** and their truncated analogs) auxiliary basis sets, were used for Cu.

```
! UKS B3LYP RIJCOSX SlowConv TightSCF def2-SV(P) def2-SV/J NORMALPRINT

%basis NewGTO 29 "def2-TZVP" end
     NewGTO 7 "def2-TZVP" end
     NewAuxGTO 29 "def2-TZV/J"  end
     NewAuxGTO 7 "def2-TZV/J"  end
     end

%scf directresetfreq 20
   diismaxeq 20
   MaxIter 700
   end

*xyz 0 1
.
.
.
*
```

SI 18.3. Representative computational input for CASSCF and MR-DDCI3 calculations.

```
! RHF AllowRHF def2-SV(P) def2-SV/J NORMALPRINT

%basis NewGTO 29 "def2-TZVP" end
    NewGTO 8 "def2-TZVP" end
    NewGTO 7 "def2-TZVP" end
    NewAuxGTO 29 "def2-TZVP/J" end
    NewAuxGTO 8 "def2-TZVP/J"  end
    NewAuxGTO 7 "def2-TZVP/J"  end
    end

%casscf
      nel 2
      norb 2
      mult 1
      NRoots 1
      MaxIter 150
      end

%mrci
      CIType    MRDDCI3
      UseIVOs  false
      IntMode  RITrafo
      Maxdim   100
      TSel              1e-8
      TPre              1e-4
      TNat              1e-4
      ETol              1e-5
      RTol              1e-5
      MaxDIIS  35
      MaxIter   100
      MaxMemInt         3000
      allsingles false
      NewBlock 1*
            NRoots 1
            excitations cisd
            Refs
             CAS(2,2)
             end
            end
      end
*xyz 0 1
.
.
.
*
```

SI 19. Coordinates from geometry optimization calculations.

Optimized Geometry of **1**

Cu	0.060734	0.179606	0.159464
O	-0.599609	-1.535859	0.373372
O	0.785890	-1.511079	0.356675
N	-1.409302	1.358709	0.031877
C	-1.259255	2.680239	-0.123533
C	-0.000996	3.319003	-0.209393
C	1.281531	2.727405	-0.149816
N	1.483235	1.412140	-0.000363
C	3.427949	0.442285	-1.156089
C	2.806875	0.864002	0.049316
C	3.442011	0.699190	1.308824
C	2.490550	3.639465	-0.257996
C	5.383110	-0.241841	0.150179
C	4.739321	0.149308	1.334028
C	4.725607	-0.102206	-1.081712
C	2.699574	0.542868	-2.476274
C	2.727589	1.069317	2.587733
C	-3.312411	0.583380	1.386668
C	-2.710728	0.763217	0.112907
C	-3.341033	0.311306	-1.076584
C	-4.616414	-0.278741	-0.971484
C	-2.584112	0.986016	2.647839
C	-2.503024	3.546920	-0.210391
C	-5.242328	-0.433665	0.274904
C	-4.588140	-0.012575	1.442646
C	-2.644370	0.429372	-2.412298
H	3.130467	3.562427	0.649016
H	2.182124	4.697314	-0.383895
H	3.134865	3.353360	-1.118553
H	-0.022554	4.410321	-0.339860
H	6.397240	-0.672124	0.189100
H	5.245439	0.018772	2.305740
H	5.220784	-0.431063	-2.011142
H	3.337335	0.181631	-3.311038
H	2.384578	1.583683	-2.710962
H	1.771765	-0.073042	-2.463270
H	3.378710	0.897513	3.471338
H	1.806620	0.455871	2.716855
H	2.402677	2.133492	2.601707
H	-5.119083	-0.630863	-1.888251
H	-1.639664	0.405966	2.759886
H	-3.209605	0.796556	3.546215
H	-2.296342	2.060981	2.649566
H	-3.153165	3.232767	-1.056726
H	-2.236179	4.614750	-0.347217
H	-3.121622	3.451161	0.709471
H	-6.239784	-0.898732	0.337700
H	-5.068483	-0.155241	2.425640
H	-3.285943	0.040460	-3.231524
H	-1.695572	-0.153706	-2.415043
H	-2.370915	1.479136	-2.658895

Optimized Geometry of **1'**

Cu	0.062529	0.178744	0.159259
O	-0.598708	-1.536354	0.373348
O	0.786805	-1.512283	0.356770
N	-1.406895	1.358579	0.031377
C	-1.256160	2.680010	-0.124205
C	0.002432	3.318120	-0.210043
C	1.284652	2.725877	-0.150270
N	1.485672	1.410530	-0.000616
C	3.429993	0.439522	-1.156034
C	2.809028	0.861725	0.049257
C	3.443969	0.696765	1.308844
C	5.384690	-0.245418	0.150502
C	4.740996	0.146225	1.334239
C	4.727367	-0.105620	-1.081466
C	-3.310518	0.584410	1.386108
C	-2.708631	0.763761	0.112375
C	-3.339062	0.312005	-1.077108
C	-4.614753	-0.277377	-0.972038
C	-5.240855	-0.431807	0.274316
C	-4.586556	-0.010887	1.442057
H	-0.018854	4.411833	-0.341081
H	6.398208	-0.676198	0.189651
H	5.253768	0.019183	2.303173
H	5.229321	-0.430318	-2.008896
H	-5.124647	-0.624972	-1.886721
H	-6.238158	-0.896338	0.337026
H	-5.074139	-0.149820	2.422261
H	-2.177169	3.289677	-0.188550
H	2.181420	3.368686	-0.233068
H	2.898947	0.547441	-2.114248
H	2.923264	1.001435	2.229349
H	-2.781373	0.912556	2.293604
H	-2.831784	0.432453	-2.046627

Optimized Geometry of **2**

Cu	0.025687	0.047517	-0.031281
O	-0.712601	-1.684482	-0.187651
N	0.607597	-1.848507	-0.107112
C	2.434061	-2.561275	1.302995
C	2.934189	-3.152695	2.472228
C	0.146780	-2.850683	2.144747
C	2.051231	-3.596682	3.474717
C	0.659070	-3.447058	3.303817
C	1.038188	-2.398939	1.141162
H	-0.936441	-2.736148	1.982712
H	-0.031292	-3.808569	4.085085
H	2.446613	-4.070809	4.388910
H	4.022954	-3.275908	2.599338
H	3.106402	-2.222680	0.498413
N	-1.461780	1.262467	-0.007997
C	-1.293528	2.586079	-0.101312
C	-0.023800	3.207712	-0.186271
C	1.259442	2.615221	-0.147391
N	1.472961	1.294195	-0.035431
C	3.449970	0.309037	-1.119017
C	2.807250	0.787869	0.054947
C	3.447408	0.724122	1.322751
C	2.459287	3.542514	-0.253260

C	5.422912	-0.229680	0.231366
C	4.763940	0.221504	1.384876
C	4.761321	-0.195052	-1.007119
C	2.731126	0.328072	-2.447694
C	2.723338	1.159555	2.576350
C	-3.343743	0.492773	1.377782
C	-2.769811	0.692677	0.093219
C	-3.441132	0.274553	-1.086721
C	-4.718587	-0.306805	-0.959441
C	-2.581263	0.867098	2.627916
C	-2.520006	3.482898	-0.124193
C	-5.313471	-0.483741	0.299186
C	-4.623431	-0.092394	1.456775
C	-2.783346	0.425431	-2.438532
H	3.097467	3.490617	0.656433
H	2.138693	4.594836	-0.394882
H	3.112047	3.254655	-1.107279
H	-0.037657	4.302628	-0.289154
H	6.451715	-0.620350	0.298084
H	5.272561	0.177198	2.363505
H	5.270509	-0.563671	-1.914125
H	3.381551	-0.063342	-3.259147
H	2.402457	1.352036	-2.732139
H	1.812468	-0.300219	-2.407481
H	3.357585	1.005371	3.475377
H	1.782189	0.581037	2.715789
H	2.426547	2.232005	2.547237
H	-5.249565	-0.632655	-1.870192
H	-1.623540	0.301699	2.696016
H	-3.176965	0.645278	3.539436
H	-2.306019	1.945169	2.653133
H	-3.206133	3.204127	-0.954505
H	-2.235477	4.548591	-0.243246
H	-3.109731	3.379705	0.813825
H	-6.314285	-0.939140	0.378879
H	-5.079698	-0.248097	2.449595
H	-3.448258	0.056800	-3.248785
H	-1.834354	-0.155515	-2.479870
H	-2.518250	1.481981	-2.665191

Optimized Geometry of **2'**

Cu	0.027353	0.046155	-0.032267
O	-0.711709	-1.685574	-0.187974
N	0.608413	-1.850160	-0.107327
C	2.434512	-2.563190	1.303120
C	2.934336	-3.154371	2.472604
C	0.147074	-2.851236	2.144914
C	2.051147	-3.597563	3.475241
C	0.659059	-3.447381	3.304237
C	1.038717	-2.400290	1.141178
N	-1.459568	1.261783	-0.009512
C	-1.290719	2.585282	-0.103346
C	-0.020709	3.206311	-0.188511
C	1.262266	2.613258	-0.149355
N	1.475187	1.292181	-0.036864
C	3.451788	0.305705	-1.119996
C	2.809245	0.785292	0.053757
C	3.449334	0.721759	1.321607
C	5.424444	-0.233363	0.230663
C	4.765639	0.218574	1.383973
C	4.762908	-0.198929	-1.007856
C	-3.341922	0.493484	1.376512
C	-2.767858	0.692621	0.091888
C	-3.439330	0.274331	-1.087908
C	-4.717050	-0.306402	-0.960438
C	-5.312054	-0.482571	0.298240
C	-4.621875	-0.091077	1.455696
H	-0.935766	-2.731764	1.984510
H	-0.031400	-3.807499	4.085926
H	2.446454	-4.070922	4.389802
H	4.022940	-3.278518	2.600232
H	3.106106	-2.226895	0.497163
H	-0.033240	4.304544	-0.284970
H	6.452663	-0.624435	0.297691
H	5.281268	0.178650	2.359366
H	5.277888	-0.565708	-1.912485
H	-5.255049	-0.628860	-1.868457
H	-6.312182	-0.938551	0.378153
H	-5.085987	-0.242053	2.445869
H	-2.198193	3.220454	-0.113594
H	2.152899	3.269414	-0.197352
H	2.921383	0.337852	-2.083985
H	2.918910	1.073030	2.219880
H	-2.786943	0.801830	2.275938
H	-2.957230	0.410237	-2.068056

Optimized Geometry of **3**

Cu	0.021395	-0.027410	-0.079640
N	1.508419	-1.240494	0.131983
N	-1.412515	-1.309677	-0.246500
C	0.083302	-3.208469	0.018002
H	0.103428	-4.306956	0.061360
C	-2.750472	-0.837641	-0.425928
N	0.658195	1.871357	-0.139843
C	1.330701	-2.569933	0.193836
N	-0.687538	1.845976	-0.091584
C	-3.179109	-0.450820	-1.725438
C	2.834579	-0.713540	0.226224
C	3.658170	-0.675003	-0.932925
C	3.144445	-1.156022	-2.272327
H	3.817137	-0.827568	-3.092266
H	3.066718	-2.267116	-2.323040
H	2.124371	-0.764887	-2.482010
C	2.530386	-3.460760	0.474962
H	3.046340	-3.149060	1.409768
H	2.221301	-4.520448	0.580589
H	3.290937	-3.397805	-0.334465
F	5.212256	3.061393	-1.767186
C	3.297246	-0.218075	1.475720
C	1.150627	2.149636	-1.445541
C	-0.397314	2.521488	2.301801
H	0.696058	2.485545	2.202630
C	2.549595	2.315110	-1.573206
H	3.186665	2.174437	-0.688465
C	5.444068	0.313753	0.422170
H	6.466000	0.719642	0.496865

C	-2.609747	2.295093	1.285193
H	-3.223798	2.080181	0.399197
C	-0.996964	2.943972	3.494222
C	4.969114	-0.170428	-0.805623
H	5.616777	-0.136947	-1.696706
C	-1.204321	2.177276	1.189874
C	-3.195452	2.734175	2.483769
C	3.096681	2.706605	-2.805234
C	-1.185013	-2.632034	-0.215629
C	2.410087	-0.267642	2.696612
H	2.877749	0.258102	3.555761
H	1.420837	0.202677	2.500128
H	2.194305	-1.313871	3.010291
C	-2.397313	3.055863	3.595659
H	-2.859559	3.421647	4.524766
C	2.268593	2.927280	-3.922643
H	2.700382	3.253247	-4.880249
C	-2.244724	-0.562241	-2.906557
H	-1.962880	-1.618958	-3.114771
H	-2.704773	-0.143654	-3.826284
H	-1.288674	-0.020915	-2.726147
C	0.315248	2.397440	-2.559664
H	-0.774284	2.330129	-2.435197
C	-2.345093	-3.584566	-0.457656
H	-2.830924	-3.375758	-1.436504
H	-2.000410	-4.638681	-0.456091
H	-3.139947	-3.474058	0.312162
F	5.169723	1.820403	-3.565818
F	-0.306883	2.356661	5.683426
C	-3.618862	-0.742720	0.696274
C	-3.145134	-1.114901	2.084068
H	-3.852715	-0.743798	2.854720
H	-3.048626	-2.217555	2.216664
H	-2.140855	-0.688281	2.300565
F	-0.502003	4.481511	5.234622
C	4.592570	2.895424	-2.956518
C	-4.936916	-0.286956	0.484715
H	-5.619711	-0.208593	1.346342
F	1.170168	3.338656	4.408239
C	-5.377101	0.092939	-0.791823
H	-6.406321	0.461680	-0.933235
C	-4.498321	0.018949	-1.884345
H	-4.840786	0.323272	-2.888281
C	-0.150023	3.284144	4.703450
C	4.606839	0.298432	1.549282
H	4.975504	0.686411	2.514422
F	0.495212	3.808306	-5.896903
F	-5.049385	3.931338	3.359444
F	-5.296239	3.007565	1.394703
F	-5.251379	1.767520	3.193036
C	-0.032503	2.956802	-4.985638
C	0.877556	2.766425	-3.789232
C	-4.700245	2.865243	2.599054
F	-1.244323	3.441946	-4.622311
F	-0.254183	1.775959	-5.623308
F	4.883014	3.974233	-3.724458

Optimized Geometry of **3'**

Cu	0.022829	-0.026031	-0.079045
N	1.510363	-1.238431	0.132920
N	-1.410526	-1.308949	-0.245667
C	0.086091	-3.207041	0.019335
C	-2.748677	-0.837526	-0.425260
N	0.658820	1.872994	-0.139660
C	1.333210	-2.567931	0.195072
N	-0.686904	1.847049	-0.091450
C	-3.177426	-0.451189	-1.724876
C	2.836293	-0.710889	0.227094
C	3.659916	-0.672268	-0.932030
F	5.212440	3.064599	-1.767090
C	3.298697	-0.214938	1.476494
C	1.151187	2.151181	-1.445402
C	-0.397067	2.523238	2.301790
C	2.550090	2.317224	-1.573048
C	5.445335	0.317564	0.422910
C	-2.609361	2.295663	1.285144
C	-0.996946	2.945741	3.494089
C	4.970639	-0.167103	-0.804791
C	-1.203881	2.178424	1.189910
C	-3.195303	2.734771	2.483594
C	3.097059	2.708668	-2.805143
C	-1.182460	-2.631202	-0.214482
C	-2.397347	3.057057	3.595443
C	2.268923	2.928731	-3.922637
C	0.315749	2.398371	-2.559616
F	5.170511	1.823176	-3.565437
F	-0.306705	2.359230	5.683457
C	-3.617154	-0.742717	0.696885
F	-0.502714	4.483893	5.234154
C	4.592874	2.898091	-2.956410
C	-4.935394	-0.287565	0.485166
F	1.169979	3.341562	4.408104
C	-5.375688	0.091847	-0.791477
C	-4.496832	0.017980	-1.883946
C	-0.150201	3.286554	4.703273
C	4.608066	0.302146	1.549991
F	0.495247	3.808543	-5.897174
F	-5.049783	3.931344	3.358916
F	-5.296162	3.007012	1.394379
F	-5.250846	1.767402	3.193000
C	-0.032141	2.957024	-4.985734
C	0.877950	2.767313	-3.789247
C	-4.700157	2.865223	2.598787
F	-1.244183	3.441735	-4.622569
F	-0.253291	1.775940	-5.623140
F	4.882889	3.976847	-3.724587
H	0.107094	-4.308523	0.061910
H	0.696774	2.472692	2.207448
H	3.186885	2.178431	-0.687970
H	6.467236	0.722536	0.497497
H	-3.223154	2.081757	0.398896
H	5.624241	-0.138953	-1.692141
H	-2.860067	3.422445	4.524478
H	2.700711	3.254645	-4.880269
H	-0.773967	2.315777	-2.439422

H	-5.623127	-0.214348	1.343621
H	-6.405045	0.459030	-0.932840
H	-4.844878	0.320853	-2.886474
H	4.981822	0.688645	2.513707
H	2.231855	-3.192472	0.363120
H	-2.480166	-0.524120	-2.574003
H	3.274210	-1.050617	-1.891076
H	2.635492	-0.243500	2.354968
H	-2.053776	-3.300218	-0.352986
H	-3.258498	-1.037735	1.694993

Optimized Geometry of **4**

Cu	-0.029722	0.020047	-0.203082
N	1.464571	1.266667	-0.172675
N	-1.498417	1.289273	-0.297319
C	-0.646732	-1.964136	-0.114832
C	0.722800	-1.831649	-0.363519
C	-4.693705	-0.132625	-1.628491
H	-5.123127	-0.445959	-2.595976
C	-2.500225	-3.116719	3.610006
H	-2.979597	-3.429198	4.552725
C	-2.837354	0.792268	-0.349331
C	-4.899035	0.146306	0.772824
H	-5.487839	0.047720	1.701224
C	-1.280066	2.611420	-0.368179
C	-1.256843	-2.323340	1.180280
C	2.780742	0.722264	-0.081235
C	1.278867	2.593163	-0.220900
C	-3.587227	0.657779	0.851259
C	4.759221	-0.211910	-1.150966
H	5.313579	-0.472312	-2.069175
C	4.605526	-0.161706	1.269607
H	5.038443	-0.381879	2.260780
C	-2.636742	-2.638284	1.225558
H	-3.232481	-2.570382	0.300507
C	-3.250496	-3.033710	2.424479
H	-4.325494	-3.279241	2.430452
C	-1.128379	-2.800051	3.583374
H	-0.529672	-2.863843	4.507967
C	-3.382562	0.385580	-1.598860
C	-2.976240	1.029345	2.182467
H	-3.695881	0.861942	3.012155
H	-2.068599	0.416814	2.385988
H	-2.649388	2.092454	2.218290
C	0.005666	3.204808	-0.319924
H	0.016832	4.303734	-0.374609
C	-5.455912	-0.244883	-0.454608
H	-6.482639	-0.644412	-0.496365
C	-0.513707	-2.409116	2.385342
H	0.562778	-2.172828	2.385778
C	3.332049	0.439272	1.199343
C	2.491689	3.510035	-0.171839
H	3.193070	3.300527	-1.010036
H	2.192456	4.577239	-0.224722
H	3.074056	3.357138	0.764192
C	3.489260	0.388875	-1.268540
C	-2.468425	3.549800	-0.516129
H	-3.171177	3.457738	0.341828
H	-2.139767	4.607048	-0.585991
H	-3.060722	3.306999	-1.426679
C	5.321384	-0.483834	0.106084
H	6.316127	-0.953275	0.178931
C	-2.567363	0.510220	-2.866004
H	-3.117686	0.098691	-3.739185
H	-2.305925	1.568025	-3.092920
H	-1.596482	-0.029292	-2.779701
C	2.881400	0.661644	-2.625366
H	3.531956	0.277706	-3.440183
H	1.879881	0.184719	-2.723658
H	2.717401	1.748323	-2.802594
C	2.553771	0.762708	2.453949
H	1.555160	0.269095	2.449870
H	3.102634	0.432162	3.361842
H	2.350988	1.852597	2.554821
H	-1.319106	-2.070006	-0.978724
H	1.093789	-1.892783	-1.393660
H	1.472813	-2.019175	0.413365

Optimized Geometry of **4'**

Cu	-0.029536	0.019226	-0.203196
N	1.464802	1.265795	-0.172898
N	-1.498182	1.288495	-0.297615
C	-0.646621	-1.964924	-0.114730
C	0.722922	-1.832516	-0.363400
C	-4.693490	-0.133441	-1.628699
C	-2.500245	-3.117007	3.610197
C	-2.837136	0.791533	-0.349602
C	-4.898868	0.145777	0.772579
C	-1.279781	2.610625	-0.368624
C	-1.256776	-2.323955	1.180409
C	2.780951	0.721354	-0.081363
C	1.279148	2.592292	-0.221281
C	-3.587043	0.657211	0.850986
C	4.759421	-0.213017	-1.150938
C	4.605670	-0.162526	1.269626
C	-2.636688	-2.638844	1.225691
C	-3.250485	-3.034108	2.424643
C	-1.128387	-2.800392	3.583562
C	-3.382329	0.384720	-1.599096
C	0.005972	3.203972	-0.320407
C	-5.455730	-0.245534	-0.454821
C	-0.513672	-2.409619	2.385499
C	3.332217	0.438490	1.199261
C	3.489485	0.387801	-1.268612
C	5.321544	-0.484815	0.106157
H	-5.128808	-0.444810	-2.594290
H	-2.979933	-3.429028	4.552966
H	-5.493844	0.049210	1.697530
H	5.320330	-0.471432	-2.065978
H	5.045525	-0.380549	2.258484
H	-3.231869	-2.572402	0.300108
H	-4.325433	-3.280412	2.431016
H	-0.529975	-2.862765	4.508479
H	0.016652	4.305863	-0.373127
H	-6.481782	-0.645932	-0.496341
H	0.561159	-2.165632	2.387253

H	6.315527	-0.955139	0.179025
H	-1.319700	-2.061338	-0.979794
H	1.095698	-1.877631	-1.393934
H	1.472687	-2.017147	0.414557
H	-2.161872	3.275660	-0.459954
H	2.176299	3.242765	-0.189894
H	-3.137747	0.956651	1.809975
H	-2.777994	0.487758	-2.514177
H	2.758992	0.693484	2.104240
H	3.037675	0.602940	-2.249527

Optimized Geometry of **5**

Cu	0.072421	-0.141949	0.160764
O	1.317900	1.434887	0.314701
O	-1.194234	1.386629	0.370112
N	1.535757	-1.397942	-0.169582
N	-1.359397	-1.484022	0.189465
N	0.760113	2.588122	0.477632
C	-1.157681	-2.793617	0.003751
N	-0.538113	2.529124	0.499174
C	-0.655302	4.988041	0.737584
C	-2.681151	-0.990274	0.408520
C	-2.696698	3.627693	0.788237
C	0.112208	-3.366776	-0.231364
C	-3.158787	-0.846785	1.739652
C	-4.765123	-0.087172	-0.460334
C	-1.298234	3.734193	0.677159
C	1.365260	-2.718156	-0.309258
C	-3.471941	-0.590647	-0.703222
C	-2.350519	-3.735605	0.049071
C	2.584090	-3.590780	-0.566514
C	2.849045	-0.840871	-0.246533
C	-2.278838	-1.207463	2.913503
C	-1.432125	6.140317	0.917726
C	2.473340	-0.453385	-2.735503
C	-4.458295	-0.338833	1.935929
C	-3.456766	4.795316	0.967851
C	-2.832750	6.051922	1.034156
C	-2.922624	-0.677603	-2.107885
C	3.622162	-0.709588	0.938903
C	3.337198	-0.377774	-1.498249
C	4.912283	-0.153201	0.839764
C	-5.262674	0.033039	0.847109
C	4.633023	0.172366	-1.550430
C	5.421738	0.279422	-0.394334
C	3.056105	-1.127718	2.276106
H	0.438158	5.050384	0.641301
H	-3.170390	2.636863	0.735525
H	0.127401	-4.456744	-0.373422
H	-5.388824	0.220924	-1.317108
H	-3.105856	-3.468690	-0.722707
H	-2.036316	-4.786751	-0.115599
H	-2.872725	-3.674149	1.029305
H	3.319001	-3.511059	0.265371
H	2.296298	-4.655915	-0.680841
H	3.122025	-3.269233	-1.485612
H	-2.802807	-1.025605	3.876513
H	-1.960740	-2.273683	2.892321
H	-1.342914	-0.604395	2.909448
H	3.006967	-0.045353	-3.620376
H	2.161577	-1.494770	-2.972922
H	1.534072	0.130062	-2.601931
H	-4.840556	-0.230213	2.965679
H	-3.434712	6.964618	1.175938
H	-3.664256	-0.313178	-2.850787
H	-1.999707	-0.062942	-2.210304
H	-2.638546	-1.716174	-2.388169
H	5.521904	-0.050626	1.754066
H	-6.278601	0.426002	1.018816
H	5.024002	0.530032	-2.518506
H	6.432927	0.714807	-0.453142
H	2.760955	-2.200708	2.296911
H	3.791669	-0.957958	3.091726
H	2.136306	-0.546901	2.515322
H	-0.933637	7.122872	0.966112
H	-4.552899	4.714229	1.059150

Optimized Geometry of **5'**

Cu	0.071061	-0.141349	0.161090
O	1.317022	1.435123	0.314863
O	-1.195123	1.387622	0.370411
N	1.534003	-1.397802	-0.169256
N	-1.361158	-1.482990	0.189951
N	0.759590	2.588535	0.477752
C	-1.159845	-2.792657	0.004307
N	-0.538653	2.529928	0.499367
C	-0.655091	4.988895	0.737631
C	-2.682752	-0.988832	0.409045
C	-2.696892	3.629163	0.788477
C	0.109859	-3.366212	-0.230840
C	-3.160274	-0.845117	1.740194
C	-4.766499	-0.085158	-0.459753
C	-1.298402	3.735236	0.677318
C	1.363102	-2.717973	-0.308841
C	-3.473481	-0.589036	-0.702679
C	2.847454	-0.841130	-0.246312
C	-1.431558	6.141415	0.917742
C	-4.459619	-0.336763	1.936509
C	-3.456600	4.797025	0.968059
C	-2.832203	6.053448	1.034253
C	3.620673	-0.710005	0.939075
C	3.335679	-0.378257	-1.498083
C	4.910956	-0.154012	0.839832
C	-5.263944	0.035283	0.847709
C	4.631666	0.171491	-1.550367
C	5.420475	0.278382	-0.394320
H	0.438374	5.051144	0.640994
H	-3.170599	2.638498	0.735467
H	0.125276	-4.459126	-0.372175
H	-5.396699	0.218219	-1.313651
H	-4.848966	-0.231627	2.964203
H	-3.433866	6.966353	1.176054
H	5.527850	-0.056113	1.750050
H	-6.279406	0.428537	1.019390
H	5.029449	0.524635	-2.517399
H	6.431636	0.713045	-0.453266

H	-0.932731	7.123805	0.965883
H	-4.552810	4.716449	1.059261
H	-2.046451	-3.456141	0.035846
H	-2.515085	-1.134233	2.583713
H	2.266994	-3.330299	-0.495269
H	-3.067321	-0.681364	-1.721815
H	3.205526	-1.047986	1.900762
H	2.703611	-0.463673	-2.395612

Optimized Geometry of **6**

Cu	-0.150770	-0.000089	-0.037391
O	0.490527	0.680270	-1.654170
O	0.490483	-0.680532	-1.654152
N	-0.934009	1.422647	1.028825
N	1.749768	-0.000090	1.408544
N	-0.934089	-1.422768	1.028834
N	-0.797181	1.277734	2.381156
N	1.340508	-0.000112	2.714710
N	-0.797252	-1.277867	2.381161
C	-2.454992	2.103896	-1.462185
C	-0.438028	3.653076	-1.271419
C	-2.698986	4.394329	-0.482469
C	-1.752948	3.180166	-0.604586
C	-1.445344	2.650390	0.783628
C	-1.610457	3.314346	2.017336
C	-1.175081	2.423605	3.005197
C	-1.110348	2.613728	4.499396
C	-0.890495	4.096139	4.849607
C	-2.386356	2.075308	5.176942
C	3.631948	1.266352	-0.655901
C	5.437932	0.000062	0.546335
C	3.942692	0.000002	0.172667
C	3.098728	-0.000040	1.434611
C	3.554953	0.000005	2.775400
C	2.403284	-0.000072	3.567363
C	2.287664	-0.000038	5.070252
C	2.925812	1.272504	5.663811
B	-0.166537	-0.000085	3.002162
C	3.632055	-1.266356	-0.655927
C	2.926603	-1.272115	5.663950
C	-1.445510	-2.650468	0.783628
C	-1.175247	-2.423711	3.005198
C	-1.753118	-3.180192	-0.604606
C	-1.610664	-3.314425	2.017331
C	-1.110578	-2.613837	4.499400
C	-2.455360	-2.103952	-1.462077
C	-0.438160	-3.652819	-1.271564
C	-2.698977	-4.394504	-0.482548
C	-0.890891	-4.096268	4.849626
C	-2.386557	-2.075283	5.176895
H	-1.796708	1.228635	-1.646563
H	-3.387563	1.755347	-0.963426
H	-2.722290	2.538893	-2.452363
H	0.315365	2.839365	-1.313851
H	-0.645378	3.998872	-2.310753
H	-0.002731	4.501575	-0.695935
H	-2.942194	4.775994	-1.500003
H	-3.648999	4.113988	0.027172
H	-2.221718	5.222221	0.089058
H	-2.000594	4.325044	2.170651
H	-0.241573	2.032074	4.879884
H	0.029270	4.493902	4.364851
H	-1.755392	4.712207	4.511456
H	-0.795263	4.218831	5.952333
H	-2.321143	2.192288	6.283387
H	-3.278926	2.634648	4.814074
H	-2.531898	0.998281	4.942835
H	4.243953	1.268346	-1.588472
H	2.556587	1.296342	-0.935924
H	3.877745	2.182453	-0.070326
H	6.054255	0.000091	-0.381697
H	5.703079	0.903626	1.141901
H	4.593761	0.000061	3.122967
H	1.209591	-0.000350	5.336945
H	2.831020	1.278634	6.774839
H	2.437336	2.188117	5.259122
H	4.008858	1.320445	5.405563
H	-0.403163	-0.000075	4.195933
H	5.703152	-0.903487	1.141893
H	4.244062	-1.268280	-1.588496
H	2.556698	-1.296432	-0.935952
H	3.877928	-2.182447	-0.070369
H	2.831817	-1.278177	6.774978
H	2.438699	-2.188078	5.259365
H	4.009679	-1.319412	5.405711
H	-2.000862	-4.325100	2.170640
H	-0.241760	-2.032267	4.879917
H	-1.797208	-1.228585	-1.646423
H	-3.387950	-1.755573	-0.963234
H	-2.722660	-2.538911	-2.452272
H	0.315078	-2.838961	-1.313991
H	-0.645517	-3.998579	-2.310909
H	-0.002665	-4.501279	-0.696171
H	-2.942185	-4.776109	-1.500105
H	-3.649004	-4.114347	0.027169
H	-2.221561	-5.222381	0.088875
H	0.028844	-4.494133	4.364898
H	-1.755845	-4.712247	4.511455
H	-0.795704	-4.218965	5.952355
H	-2.321397	-2.192258	6.283344
H	-3.279169	-2.634538	4.814000
H	-2.531984	-0.998244	4.942770

Optimized Geometry of **6'**

Cu	-0.001736	-0.013285	0.007882
O	1.675626	0.661739	-0.460012
O	1.672152	-0.699055	-0.456817
N	-1.320965	1.412829	0.024956
N	-0.004966	-0.007628	2.395921
N	-1.328200	-1.432569	0.031630
N	-2.315992	1.272618	0.951662
N	-1.292909	-0.003304	2.859327
N	-2.322487	-1.282968	0.957654
C	-1.431582	2.639537	-0.533514
C	-2.512561	3.307673	0.079033
C	-3.038662	2.420493	1.025061

C	0.789592	-0.007003	3.486357
C	-0.002828	-0.002181	4.660199
C	-1.329840	0.000052	4.221361
B	-2.432786	-0.002830	1.832441
C	-1.445057	-2.661290	-0.521105
C	-3.050993	-2.426794	1.036397
C	-2.529407	-3.321058	0.094548
H	-2.871018	4.321082	-0.143406
H	0.347604	-0.000562	5.701101
H	-3.519234	0.001323	2.406696
H	-2.892927	-4.333666	-0.123274
H	-0.725692	2.957095	-1.309756
H	-3.884259	2.497832	1.717464
H	1.880986	-0.010026	3.366167
H	-2.286705	0.003746	4.756899
H	-0.740744	-2.986078	-1.295784
H	-3.896980	-2.496499	1.729138

Optimized Geometry of **7**$^{+}$

Cu	0.097342	-0.132293	-0.097922
C	-1.687267	-0.979427	-0.447650
C	-0.778169	-2.000187	-0.156961
N	2.036366	2.053671	1.190443
N	-0.025526	1.839577	-0.045421
N	2.040117	-0.158077	0.216064
C	0.832802	2.596972	0.687774
C	0.513941	3.955552	0.963680
C	-0.638424	4.524174	0.421953
C	-1.479171	3.747617	-0.396151
C	-1.132279	2.414785	-0.587592
C	2.711837	0.877171	0.785465
C	4.111068	0.773184	1.011020
C	4.797280	-0.377596	0.623362
C	4.094322	-1.430355	0.010779
C	2.724326	-1.269031	-0.166600
C	2.760807	2.887514	2.146880
C	2.590815	2.669005	3.534677
C	1.666485	1.590652	4.096319
C	2.451111	0.540650	4.913598
C	0.517794	2.206434	4.925611
C	3.325781	3.507674	4.406740
C	4.182698	4.509380	3.926293
C	4.333048	4.705676	2.540415
C	3.618926	3.890260	1.651676
C	-0.612253	-2.688976	1.139445
C	0.187026	-3.857606	1.192033
C	0.364865	-4.557024	2.397179
C	-0.252411	-4.099271	3.575253
C	-1.051739	-2.939122	3.536854
C	-1.231215	-2.240657	2.333875
H	1.175490	4.569136	1.585560
H	-0.871717	5.580048	0.633375
H	-2.390472	4.155980	-0.857480
H	-1.763455	1.746285	-1.190974
H	4.662330	1.599715	1.473968
H	5.883824	-0.444631	0.793005
H	4.590560	-2.356298	-0.315541
H	2.119340	-2.059488	-0.633343
H	1.203665	1.060275	3.235263
H	3.262698	0.077679	4.309730
H	1.769347	-0.271026	5.252573
H	2.914283	0.992697	5.819521
H	-0.069382	2.938070	4.327472
H	0.903772	2.733224	5.827344
H	-0.177318	1.409400	5.272609
H	3.222506	3.371489	5.496329
H	4.737857	5.142167	4.638473
H	5.004253	5.489435	2.153108
H	3.719982	4.023874	0.562176
H	-2.413748	-0.625583	0.294711
H	-1.921198	-0.755688	-1.496359
H	-0.297505	-2.502169	-1.011382
H	0.664899	-4.227071	0.268817
H	0.987779	-5.466997	2.415065
H	-0.114236	-4.645546	4.523219
H	-1.542263	-2.576870	4.455826
H	-1.862632	-1.337098	2.326351

Optimized Geometry of **8**

Cu	-0.053611	0.067911	-0.135470
N	1.435421	1.305839	-0.162265
N	-1.527161	1.333364	-0.300228
N	-0.483586	-1.915930	-0.079994
C	0.840571	-1.720037	-0.108356
C	-4.761530	-0.178753	-1.412400
C	-2.483292	-3.530333	3.310945
C	-2.877217	0.864065	-0.279172
C	-4.943352	0.427503	0.931080
C	-1.300057	2.643060	-0.480494
C	-1.102545	-2.426819	1.090716
C	2.755522	0.773198	-0.034006
C	1.253657	2.627910	-0.301271
C	-3.618348	0.910570	0.933522
C	4.754454	-0.178748	-1.046648
C	4.578654	-0.025393	1.368700
C	-2.507889	-2.297658	1.206478
C	-3.185671	-2.833017	2.310401
C	-1.092432	-3.697024	3.185263
C	-3.437660	0.303332	-1.458871
C	-2.982896	1.424611	2.205725
C	-0.012302	3.234529	-0.467288
C	-5.517971	-0.110456	-0.231145
C	-0.404842	-3.156264	2.087830
C	3.297098	0.552106	1.262413
C	2.468785	3.542179	-0.282975
C	3.476981	0.398653	-1.200833
C	-2.478533	3.572682	-0.729425
C	5.309077	-0.386442	0.225574
C	-2.617034	0.208829	-2.724188
C	2.881581	0.609535	-2.574498
C	2.499764	0.910734	2.495046
H	-5.203727	-0.614282	-2.325142
H	-3.019107	-3.960298	4.173742
H	-5.527156	0.466437	1.867159
H	5.320330	-0.471483	-1.947842
H	5.006371	-0.195913	2.371809

H	-3.057968	-1.777122	0.408135
H	-4.280116	-2.712223	2.381674
H	-0.533258	-4.267697	3.946825
H	-3.687157	1.347186	3.061750
H	-2.069032	0.839653	2.456838
H	-2.658711	2.486311	2.124392
H	0.005226	4.324726	-0.610800
H	-6.553791	-0.487611	-0.214653
H	0.677703	-3.336867	1.991114
H	3.192038	3.277852	-1.085784
H	2.173619	4.603676	-0.413643
H	3.023898	3.450323	0.677147
H	-3.186650	3.582573	0.128694
H	-2.137353	4.612244	-0.910601
H	-3.069037	3.238198	-1.611446
H	6.310041	-0.837044	0.326858
H	-3.206283	-0.243182	-3.550849
H	-2.251755	1.203517	-3.063179
H	-1.711903	-0.419705	-2.560411
H	3.527903	0.168122	-3.362938
H	1.869568	0.152321	-2.656143
H	2.744382	1.688561	-2.811595
H	1.527889	0.366193	2.519854
H	3.060406	0.660793	3.421322
H	2.242391	1.992885	2.530479
H	1.332299	-1.716558	-1.093512
H	1.498582	-1.879719	0.764615

Optimized Geometry of $[Me_2NN]Cu(\kappa^1\text{-}N\text{-}PhN{=}CH_2)$

Cu	-0.252695	0.165524	-0.157162
N	1.280760	1.332886	0.007227
N	-1.658589	1.503002	-0.395418
N	-0.601114	-1.714717	-0.200311
C	-0.955048	-2.426984	-1.223556
C	-4.756140	0.123739	-1.968401
C	-0.656837	-3.602103	3.609013
C	-2.986550	1.018989	-0.547329
C	-5.075703	0.234537	0.433724
C	-1.380108	2.811458	-0.430232
C	-0.629872	-2.359884	1.084551
C	2.545285	0.730401	0.266177
C	1.164277	2.664744	-0.106230
C	-3.791256	0.788105	0.604966
C	4.531366	-0.438444	-0.529199
C	4.217483	-0.073251	1.848781
C	-1.802459	-2.995897	1.543569
C	-1.812024	-3.609769	2.807536
C	0.509826	-2.965115	3.145689
C	-3.464847	0.676636	-1.844988
C	-3.261817	1.115935	1.982012
C	-0.067781	3.337505	-0.307219
C	-5.563984	-0.094212	-0.841485
C	0.525633	-2.333052	1.892501
C	2.991302	0.581344	1.611522
C	2.420391	3.520824	-0.026830
C	3.312964	0.209261	-0.814056
C	-2.520056	3.802690	-0.609183
C	4.990394	-0.577151	0.790540
C	-2.595371	0.901225	-3.061413
C	2.810390	0.338101	-2.232983
C	2.147323	1.091816	2.757351
H	-5.129965	-0.140322	-2.973202
H	-0.667990	-4.084152	4.600352
H	-5.703342	0.057996	1.324859
H	5.129590	-0.841284	-1.364815
H	4.568151	-0.187543	2.889642
H	-2.712061	-2.973242	0.921151
H	-2.735217	-4.091912	3.170291
H	1.420295	-2.954742	3.767766
H	-3.041369	2.201000	2.100295
H	-3.989410	0.827150	2.770970
H	-2.302162	0.586629	2.181663
H	0.004871	4.433274	-0.378601
H	-6.572007	-0.526107	-0.955794
H	1.433623	-1.830264	1.520259
H	3.156642	3.221679	-0.806248
H	2.186063	4.597154	-0.162147
H	2.938311	3.397322	0.950351
H	-2.148959	4.847850	-0.645187
H	-3.090477	3.601479	-1.543446
H	-3.254258	3.722368	0.224555
H	5.948546	-1.082823	0.995125
H	-3.075365	0.494604	-3.977393
H	-2.386933	1.980803	-3.236644
H	-1.597161	0.421282	-2.941801
H	3.483679	-0.181237	-2.948359
H	1.788123	-0.095041	-2.333440
H	2.720330	1.400584	-2.552265
H	1.123904	0.653307	2.728497
H	2.608724	0.839327	3.736545
H	2.005108	2.195338	2.721147
H	-0.994396	-1.959293	-2.213415
H	-1.206752	-3.493727	-1.121840

Optimized Geometry of **9**

Cu	0.064176	0.053543	0.209639
F	-1.174734	-1.244791	0.387737
F	1.353978	-1.198687	0.353499
N	-1.389987	1.300159	0.067036
C	-1.244524	2.620668	-0.081922
C	0.000642	3.272000	-0.165641
C	1.270411	2.665906	-0.120559
N	1.467600	1.352222	0.028556
C	3.406526	0.426494	-1.161361
C	2.792021	0.822932	0.058523
C	3.471673	0.724776	1.304332
C	2.482917	3.570299	-0.258113
C	5.445861	-0.069814	0.096460
C	4.808761	0.286173	1.296370
C	4.744356	-0.006751	-1.118777
C	2.625388	0.438748	-2.452392
C	2.760256	1.047378	2.595508
C	-3.340496	0.582844	1.379782
C	-2.693140	0.722014	0.120686
C	-3.320413	0.319947	-1.090757
C	-4.640377	-0.162548	-1.024539

C	-2.612179	0.915987	2.658517
C	-2.493023	3.481602	-0.172739
C	-5.311300	-0.267551	0.204982
C	-4.660474	0.095463	1.395335
C	-2.571915	0.381366	-2.399575
H	3.153599	3.480432	0.624557
H	2.174136	4.630224	-0.365959
H	3.093511	3.285776	-1.143594
H	-0.021130	4.362825	-0.291786
H	6.491892	-0.417818	0.110485
H	5.352497	0.210433	2.253267
H	5.238325	-0.313162	-2.056312
H	3.260889	0.125075	-3.307605
H	2.205440	1.442536	-2.686310
H	1.762107	-0.262107	-2.386332
H	3.442775	0.939828	3.465311
H	1.899267	0.356864	2.742682
H	2.347892	2.081146	2.608548
H	-5.144567	-0.473282	-1.955138
H	-1.721170	0.258656	2.774430
H	-3.268774	0.769302	3.542361
H	-2.241270	1.965257	2.676448
H	-3.123796	3.180091	-1.038092
H	-2.226863	4.552901	-0.282552
H	-3.126903	3.360279	0.732830
H	-6.343725	-0.652795	0.237183
H	-5.179362	-0.012722	2.362795
H	-3.215640	0.055752	-3.244093
H	-1.680344	-0.285245	-2.366667
H	-2.196936	1.404062	-2.627398

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