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X-ray Absorption Edge Spectroscopy and Computational Studies on LCuO_2 Species:

Superoxide- Cu^{II} versus Peroxide- Cu^{III} Bonding

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Abstract

The geometric and electronic structures of two mononuclear CuO_2 complexes $[\text{Cu}(\text{O}_2)\{\text{HB}(3\text{-Ad-5-Prpz})_3\}]$ (**1**) and $[\text{Cu}(\text{O}_2)(\beta\text{-diketiminate})]$ (**2**) have been evaluated using Cu K- and L- edge X-ray absorption spectroscopy studies in combination with valence bond configuration interaction (VBCI) simulations and spin unrestricted broken symmetry density functional theory (DFT) calculations. Cu K- and L-edge XAS data indicate the Cu(II) and Cu(III) nature of **1** and **2**, respectively. Total integrated intensity under the L-edges show that the ψ_{LUMO}^* 's in **1** and **2** contain 20% and 28% Cu character, respectively, which are indicative of very covalent ground states in both complexes, although more so in **1**. Two state VBCI simulations also indicate that the ground state in **2** has more Cu ($|3d^8\rangle$) character. DFT calculations show that the ψ_{LUMO}^* in both complexes is dominated by $\text{O}_2^{\text{n-}}$ character, although the $\text{O}_2^{\text{n-}}$ character is higher in **1**. It is shown that the ligand L plays an important role in modulating Cu-O₂ bonding in these LCuO_2 systems and tunes the ground states of **1** and **2** to have dominant Cu(II)-superoxide like and Cu(III)-peroxide like character, respectively. Ligand field and $Q_{\text{Mol}}^{\text{M}}$ (charge on the absorbing atom in the molecule) contributions to L- and K-edge energy shifts are evaluated using DFT and TD-DFT calculations. It is found that the ligand field makes a dominant contribution to the edge energy shift, while the effect of $Q_{\text{Mol}}^{\text{M}}$ is minor. The charge on the Cu in the Cu(III) complex is found to be similar to that in Cu(II) complexes, which indicates a much stronger interaction with the ligand leading to extensive charge transfer.

Keywords

XAS; K-edge; L-edge; copper; peroxide; superoxide

Introduction

Copper containing enzymes play important roles in O_2 activation and reduction in biological systems. These include the trinuclear Cu site in laccase,¹ the binuclear Cu proteins and the

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heteronuclear heme-Cu_B site present in cytochrome *c* oxidase.² The group containing the binuclear Cu sites is further divided into exchange-coupled and non-coupled classes on the basis of the magnetic interactions between the two copper sites.³ The coupled binuclear proteins, which include hemocyanin, tyrosinase, and catechol oxidase, exhibit strong magnetic coupling ($-2J \leq 1200 \text{ cm}^{-1}$) and have been extensively studied using spectroscopic techniques.⁴⁻⁷ Insight into the geometric and electronic structure of these sites has also been gained by studies on complexes, that model the protein function of O₂ binding and activation to functionalize organic substrates.

Relative to the exchange coupled proteins, less is known about the geometric and electronic structure of the non-coupled binuclear copper proteins. These include dopamine β -monooxygenase (D β M) and peptidylglycine α -hydroxylating monooxygenase (PHM), which utilize molecular O₂ to catalyze C-H bond hydroxylation in a stereospecific fashion (dopamine to norepinephrine in D β M and glycine backbone C-H hydroxylation in PHM).^{8,9} Crystal structures of PHM have been solved and show that the Cu $\cdots$ Cu separation is $\sim 11 \text{ \AA}$. This large separation precludes electronic coupling of the two copper centers.^{8,10} The two Cu atoms are labeled Cu_M (ligated by S(Met) and two N(His)) and Cu_H (ligated by three N(His)). O₂ binding and reduction occurs at Cu_M while Cu_H transfers one electron to the Cu_M site to complete the two electron reduction of O₂ required for the reaction. It has been shown that the copper atoms cycle between a Cu_M^ICu_H^I form and a Cu_M^{II}Cu_H^{II} form in the reaction mechanism. Although various experimental and theoretical studies have been performed on both PHM and D β M,^{3, 11-14} the mechanism of the long range electron transfer from Cu_H to Cu_M and O₂ reduction is unclear. Various mechanisms have been proposed, including superoxide channeling,¹⁵ substrate binding mediated electron transfer to generate a hydroxide intermediate for two electron reduction of O₂^{16,17} and direct H-atom abstraction by a one electron reduced superoxide intermediate.^{5,11,12}

Recently, the Cu_M(O₂) (plus slow substrate) intermediate has been trapped and the crystal structure determined (Figure 1).¹⁸ This has triggered interest in characterizing synthetic models using spectroscopic methods which help understand various aspects of the protein chemistry. Two model complexes have been structurally characterized, [Cu(O₂){HB(3-*i*Bu-5-*i*Prpz)₃}], [HB(3-*i*Bu-5-*i*Prpz)₃ = hydrotris(3-*tert*-butyl-5-isopropyl-1-pyrazolyl) borate], **1**¹⁹ and [Cu(O₂)(β -diketiminate)] [β -diketiminate=*N,N'*-bis(2,6-diisopropylphenyl) 2,2,6,6-tetramethyl-3,5-pentanediiiminate], **2**²⁰ (Figure 2). A variation of **2** with an anilido-imine ligand system has also been structurally characterized,²¹ and the results corroborate the structural data for **2**. Spectroscopic and theoretical characterization of **1** elucidated some aspects of O₂ binding and activation by a single copper center.²² **2** is structurally similar to **1** in that it also has a side-on (ν^2) binding mode of O₂ to Cu. However, these molecules differ dramatically in their spectroscopic properties. **1** has been described using magnetic susceptibility, electronic absorption, vibrational spectroscopy and DFT calculations as a highly covalent singlet species with no spin polarization in the ground state. The O-O stretching frequency in **1** is 1043 cm^{-1} which is similar to that of well characterized superoxide species.^{23,24} In contrast, **2** has an O-O stretching frequency at 948 cm^{-1} indicating considerable peroxide (O₂²⁻) character.^{20,25} Cu K-edge X-ray absorption studies on **2** indicate that the copper is in the +3 oxidation state.²⁶ DFT calculations support the resonance Raman studies and indicate that **1** and **2** have predominant peroxide and superoxide like character, respectively.^{20,22,26,27} These differences in two structurally analogous molecules hold potentially important information on O₂ binding and activation by the mononuclear Cu_M site.

Cu L-edge X-ray absorption spectroscopy is a direct probe of the Q_{Mol}^M (charge on the absorbing metal(M) in a molecule) and ligand field of the Cu center.^{28,29} L edges are associated with the 2p $\rightarrow$ 3d transition and have significant intensity due to their electric dipole allowed nature ($\Delta l = +1$). For Cu this transition occurs at $\sim 930 \text{ eV}$. Additionally, relative to Cu K-edges ($\sim$

9000 eV), the resolution at ~930 eV is much higher (0.1 eV compared to ~1 eV), which results in sharp, well separated peaks.³⁰ In the case of most d^n ($n < 9$) species, the L-edge spectrum is rich in multiplet structure.³¹ To interpret the L-edge spectra, the atomic terms need to be evaluated for both the initial and final configurations. In a molecular system the atomic Hamiltonian is combined with ligand field terms using perturbation theory (see Experimental Section for details). Finally, the L-edges of highly covalent systems need an additional charge transfer term in the Hamiltonian to include the effects of ground state covalency and electronic relaxation due to the $2p \rightarrow 3d$ excitation.

In this study, our Cu K-edge study of **2**²⁶ has been extended to include the Cu K-edge of **1** and the Cu L-edges of **1** and **2**. These data are analyzed with a valence bond configurational interaction (VBCI) model, density functional and TD-DFT^{32,33} calculations to understand the electronic structures of these molecules. The role of the ligand L in tuning these $LCuO_2$ systems towards more superoxide- or peroxide-like character has been explored. The comparison of **1** and **2** provides insight into the electronic structure of a Cu(III) site in a highly covalent ligand environment. This study utilizes metal K- and L-edge spectroscopies to understand the changes in Q_{Mol}^M and ligand field of the metal center upon a one electron oxidation of Cu(II) species.

2. Experimental Section

2.1. Samples

$[Cu(O_2)\{HB(3-Ad-5-^iPrpz)_3\}]$, $[HB(3-Ad-5-^iPrpz)_3] = \text{hydrotris(3-adamantyl-5-isopropyl-1-pyrazolyl)borate} = (^1L)^{34}$ and $[Cu(O_2)(\beta\text{-diketiminate})] [\beta\text{-diketiminate} = N,N'\text{-bis(2,6-diisopropylphenyl)-3,5-methyl-diiminato} = (^2L)]$, have been studied as analogues of **1** and **2** since they have greater thermal stability. The $[^1LCu(O_2)]$ **1**¹⁹ and $[^2LCu(O_2)]$ **2**²⁶ complexes were synthesized as previously described. Both complexes are temperature sensitive (rate of decomposition highly enhanced above ~ -40 °C) and were handled in a glove bag under inert N_2 atmosphere and at dry ice temperatures during sample preparation. For Cu K-edge X-ray absorption (XAS), the solid samples were finely ground with BN into a homogeneous mixture and pressed into a 1 mm aluminum spacer between X-ray transparent Kapton tape. The samples were immediately frozen and stored under liquid N_2 . During data collection, the samples were maintained at a constant temperature of 10 K using an Oxford Instruments CF 1208 liquid helium cryostat. The Cu L-edge samples were similarly treated and spread thinly over double sided adhesive conducting graphite tape on an Al sample paddle. The paddles were transferred onto a magnetic manipulator in an antechamber pre-chilled with liquid N_2 and then transferred into the main chamber and affixed to an Al block which was cooled through conduction by a continuous flow of liquid He into a Cu block in an internal cavity. The temperature was monitored using a Lakeshore temperature controller and maintained at 20 K during the course of data measurement. The samples were positioned at 45° to the incident beam. The room temperature stable $[Cu(TMPA)(OH_2)](ClO_4)_2$ ³⁵ complex **3**, included as a reference, was handled on the bench top. The Cu K- and L- edge data for all samples were collected at similar temperatures.

2.2. X-ray Absorption Spectroscopy

2.2.1 Cu K-edge—The Cu K-edge X-ray absorption spectra of **1**, **2** and **3** were measured at the Stanford Synchrotron Radiation Laboratory (SSRL) on the focused 16-pole 2.0 T wiggler beam line 9-3 and the unfocused 8-pole 1.8 T wiggler beam line 7-3 under standard ring conditions of 3 GeV and 60-100 mA. A Si(220) double crystal monochromator was used for energy selection. A Rh-coated harmonic rejection mirror and a cylindrical Rh-coated bent focusing mirror were used for beam line 9-3 whereas the monochromator was detuned 50% at 9987 eV on beam line 7-3 to reject components of higher harmonics. Transmission mode was used to measure data to $k = 16 \text{ \AA}^{-1}$. Internal energy calibration was accomplished by

simultaneous measurement of the absorption of a Cu-foil placed between two ionization chambers situated after the sample. The first inflection point of the foil spectrum was fixed at 8980.3 eV. Data presented here are 2-4 scan average spectra, which were processed by fitting a second-order polynomial to the pre-edge region and subtracting this from the entire spectrum as background. A three-region spline of orders 2, 3 and 3 was used to model the smoothly decaying post-edge region. The data were normalized by subtracting the cubic spline and assigning the edge jump to 1.0 at 9000 eV using the *SPLINE* routine in the XFIT³⁶ suite of programs.

2.2.2 Cu L-edge—Cu L-edge X-ray absorption spectra were recorded at SSRL on the 31-pole wiggler beam line 10-1 under ring operating conditions of 50-100 mA and 3 GeV with a spherical grating monochromator with 1000 lines/mm and set at 30 μ m entrance and exit slits. Sample measurements were performed using total electron yield mode where the sample signal (I_1) was collected with a Galileo 4716 channeltron electron multiplier aligned to 45° relative to the copper paddle. The signal was flux normalized (I_1/I_0) using the photocurrent of a gold-grid reference monitor (I_0). Data for all samples were recorded in a sample chamber maintained below 10⁻⁶ Torr, isolated from the UHV beam line by a 1000 Å Al window. External energy calibration was accomplished by L-edge measurements on CuF₂ before and after the sample. The L₃ and L₂ peak maxima were assigned to 930.5 eV and 950.5 eV, respectively. The variance in this calibration energy measured prior to and after each sample scan was used to linearly shift the experimental spectra between calibration scans. Spectra presented here are 3-5 scan averages, which were processed by fitting a second-order polynomial to the pre-edge region and subtracting it from the entire spectrum as background, resulting in a flat post-edge. The data were normalized to an edge jump of 1.0 at 1000 eV. The data for **3** were fit using *EDG_FIT*.³⁷ The L₃ and L₂ pre-edges were modeled using 50:50 Lorentzian:Gaussian Pseudo-Voigt band shapes and the rising edges were modeled using arctangents. The total pre-edge intensity was calculated as L₃ + L₂. Fits to the data for **1** and **2** were more complicated due to the presence of shakeup transitions. Two arctangents were subtracted from the data which were separated by 3/2* $\lambda_{L,S}$ (20.25 eV) and fixed with an L₃:L₂ intensity ratio of 2:1. The total integrated area was obtained between 930-950 eV. The total integrated area of the L-edge of **3** was also obtained for comparison to **1** and **2**.

2.3. Electronic Structure Calculations

Gradient-corrected, (GGA) spin-unrestricted, broken symmetry, density functional calculations were carried out using the Gaussian03³⁸ package on a 2-cpu linux computer. In reference²² Chen *et. al.* have found that a more reasonable description of **1** was obtained using the BP86 pure functional, which gives the correct energy ordering of the singlet and low lying triplet excited state. Thus, the Becke88^{39,40} exchange and Perdew86⁴¹ correlation non-local functionals with Vosko-Wilk-Nusair local functionals⁴² as implemented in the software package (BP86) were employed in this study to compare the electronic structure differences between **1** and **2**. The triple- ζ 6-311+G* and the double- ζ 6-31G*⁴³⁻⁴⁵ basis sets were used on the Cu, O and N atoms and the C and H atoms respectively. Population analyses were performed by means of Weinhold's Natural Population Analysis (NPA)⁴⁶⁻⁴⁸ including the Cu 4p orbitals in the valence set. Wave functions were visualized and orbital contour plots were generated in Molden.⁴⁹ Compositions of molecular orbitals and overlap populations between molecular fragments were calculated using the AOMix program.^{50,51} For **1** the alkyl side chains on the pyrazole rings were replaced by hydrogen atoms. For **2** the isopropyl side chains on the benzene rings on the ligand and the methyl groups on the carbon backbone were replaced by hydrogen atoms.

The geometry optimization of the reference complexes $[\text{Cu}^{\text{II}}\text{L}]^{2-}$ and $[\text{Cu}^{\text{III}}\text{L}]^{-}$ and the single point calculation on $[\text{Cu}^{\text{III}}\text{L}^*]^{-}$ (For L see section 4.2.5) employed the BP86 functional with 6-311G* basis sets on Cu and N and 6-31G* basis sets on the rest of the atoms.

2.4. XAS Multiplet Calculations

Atomic multiplet calculations were carried out using the T.T Multiplet software package developed by R. D. Cowan *et. al.*⁵² and modified by B. T. Thole. The output of an atomic multiplet calculation is subjected to a ligand-field (LF) multiplet calculation which applies an electrostatic field around the metal center and employs Butler's branching rules⁵³ to split the atomic multiplets. Covalency was then included through charge transfer mixing using a two configuration valence bond configuration interaction (VBCI) model (program developed by Okada).⁵⁴ Atomic Slater integrals were used in all simulations.⁵⁵ With the inclusion of electronic relaxation ($Q-U = -2$ eV)(see section 4.1), the charge transfer parameters model the shakeup intensity observed at higher energies relative to the main L_3 and L_2 pre-edge peaks. The plots were generated using the program integrated with the multiplet program. The spectral simulations were generated using a 0.4 and 0.6 eV Lorentzian broadening contributions (to account for core-hole life time effects) to the L_3 and L_2 edges, respectively. The whole spectrum was then convoluted with a 0.4 eV Gaussian (to account for experimental broadening).

2.5. TD-DFT Calculations

The time-dependent density functional (TD-DFT) framework implemented in ORCA^{56,57} was used to compute Cu K-edge, $1s \rightarrow 3d$, and Cu L-edge, $2p \rightarrow 3d$, transition energies. The Becke88 exchange and Perdew86 correlation non-local functionals were employed. The all-electron Gaussian basis sets used were those reported by the Ahlrichs group. Accurate triple- ξ valence basis sets (TZV(P))^{58,59} with one set of polarization functions on all the atoms were used to perform spin unrestricted single point calculations. The basis set dependence was tested by repeating the calculations using 6-311G*⁶⁰⁻⁶² with polarization. The self consistent field (SCF) calculations were set to a tight convergence criterion (10^{-7} Eh in energy, 10^{-6} Eh in the density change and 10^{-6} in the maximum element of the DIIS error vector). The RI modification was not employed. The input structures for the TD-DFT calculation were obtained from the spin unrestricted DFT calculations performed at the BP86 level in Gaussian using a 6-311G* basis set on the Cu and O atoms and 6-31G* basis set on N, C and H atoms.

3. Results

3.1. Cu K-edge

The normalized Cu K-edge X-ray absorption spectrum of **1** compared to that of **2** is presented in Figure 3. The pre-edge and shakedown energies are given in Table 1. In a previous study the Cu K-edge spectrum of **2** was used to determine the predominant Cu(III) character of the complex.²⁶ The Cu(II) K-edge consists of a weak pre-edge transition at ~ 8979 eV before the onset of the rising edge. The pre-edge corresponds to a dipole-forbidden quadrupole-allowed $1s \rightarrow 3d$ transition which can gain intensity through $4p$ mixing into the $3d$ orbitals if the molecule deviates from centrosymmetry.⁶³ In **2** the pre-edge transition in the Cu K-edge was observed at ~ 8980.7 eV, ~ 2 eV higher in energy than observed for Cu(II) complexes, thus falling in the Cu(III) region. In **1**, the pre-edge occurs at 8978.6 eV demonstrating its Cu(II) nature.⁶⁴ To higher energy in the Cu K- near-edge region, an intense $1s \rightarrow 4p$ + ligand to metal charge transfer (LMCT) shakedown transition is observed in **2** (8986.5 eV) which reflects the strong covalent bonding between the metal and ligand orbitals usually associated with Cu(III) complexes.^{65,66} In contrast, in **1**, this shakedown transition occurs at 8988.3 eV and is weaker, leading to an almost featureless rising edge reflecting predominant Cu(II) character.

3.2. Cu L-Edge

The normalized Cu L-edge X-ray absorption spectra of **1**, **2** and the reference complex D_{4h} $(C_4H_8N_3O)_2[CuCl_4]^{2-}$ are presented in Figure 4A. The expanded L_3 regions of the spectra of **1** and **2** are compared to the spectrum of $La_2Li_{1/2}Cu_{1/2}O_4$, an inorganic Cu(III)-oxide **4** (spectrum adapted from ref ²⁹) in Figure 4B. The Cu L-edge spectrum involves the Cu $2p \rightarrow 3d$ transition and consists of two peaks split by ~ 20 eV ($3/2 \times$ the $2p$ core spin orbit coupling) with an intensity ratio of $\sim 2:1$ [$J=3/2$ and $1/2$ corresponding to the L_3 (~ 930 eV) and L_2 edge (~ 950 eV), respectively].⁶⁷ The L_2 edge is broadened due to an additional Auger decay channel (Coster-Kronig)⁶⁸ of the excited state, which is absent for the L_3 edge. Both these pre-edge features are followed by weak $2p \rightarrow 4s$ and $2p \rightarrow$ continuum edge transitions (the intensity of the $\Delta l = +1$ transition is ~ 30 times higher than the $\Delta l = -1$ transition) at ~ 10 eV higher energy. In the case of Cu(II) $3d^9$ and Cu(III) $3d^8$ complexes, multiplet effects do not redistribute the intensity between the L_3 and L_2 edges (see Supporting Information). Hence, we focus on the L_3 edge energy positions (an analogous trend is observed in the energy shifts in the L_2 edge). The L_3 edge of **1** and D_{4h} $[CuCl_4]^{2-}$ occur at 930.8 eV and 931 eV,²⁹ respectively, which are in the range generally observed for normal Cu(II) complexes. The L_3 edge of **2** is at 932.7 eV, which is comparable in energy to that of **4** (~ 932.9 eV). This ~ 2 eV shift in the pre-edge is consistent with a change in oxidation state on the Cu and further supports the assignment of **2** as having predominantly Cu(III) character.

Due to the localized nature of the Cu $2p$ orbital and the fact that a $p \rightarrow d$ transition is electric-dipole allowed, the L-edge transition decreases in intensity as the d orbital mixing with the ligand (covalency) increases. This provides a direct probe of Cu $3d$ ($1-\beta^2$) character in the

$$\psi_{\beta-LUMO}^* = [1 - \beta^2]^{1/2} |Cu(3d_{x^2-y^2})\rangle - \beta |Ligand(np)\rangle$$

Correlation of the L-edge intensity under the L_3+L_2 peaks with that in D_{4h} $[CuCl_4]^{2-}$ gives a quantitative estimate of the amount of Cu character in an unknown complex.⁷⁰ Figure 4A shows a comparison of the total intensity under the L-edge spectra of D_{4h} $[CuCl_4]^{2-}$, **1** and **2**. Since both **1** and **2** have two unoccupied spin orbitals (α and β spin of the $3d_{x^2-y^2}$ orbital) with significant Cu character (*i.e.*, two-hole systems) in contrast to the one unoccupied orbital in D_{4h} $[CuCl_4]^{2-}$ (β spin of the $3d_{x^2-y^2}$ orbital) a normalization factor of $1/2$ has to be used to quantitatively compare the covalencies of each hole in **1**, **2** and D_{4h} $[CuCl_4]^{2-}$. Thus, the per-hole L-edge intensities of **1** and **2** ($1/2$ of the intensity in Figure 4A) are much lower than that of D_{4h} $[CuCl_4]^{2-}$ indicating very covalent Cu centers in both complexes. Since the high covalency also leads to shakeup satellite features on the L-edge which redistribute the intensity (*vide infra*),⁷¹ the total integrated areas were obtained for **1** and **2** and compared to that of D_{4h} $[CuCl_4]^{2-}$.⁷² The Cu characters obtained from these total integrated areas are given in Table 1. The reduced Cu character in both of the $[LCuO_2]$ complexes indicates very strong mixing of the O_2^{n-} ligand with the empty Cu d orbital. Further, the total integrated intensity for **2** (which quantitates to 28% per-hole metal d -character) is more than that of **1** (20%) indicating that **2** has more Cu character, consistent with its Cu(III) description.²²

4. Analysis

4.1. Multiplet Calculations

Both **1** and **2** are two-hole systems which can lead to multiplet effects on the L-edge. To gain further insight into the differences in bonding in the two monomeric $[LCuO_2]$ complexes, the TT-Multiplets program was used to fit the multiplets observed in the L-edge data. The atomic multiplets were simulated by setting the covalent reduction of electron repulsion, β at 80%. Note that the multiplet splitting is observed in the low intensity high energy satellite peak ($\sim$

940 eV feature) (Figure 4B Inset) while the main peak is featureless. This indicates that an inverted bonding description is required for the final state (see below). In this case the ligand field effects alone are limited and contained mostly within the low intensity satellite peaks. Thus, the data were fit by simultaneously optimizing the ligand field and charge transfer (see below) parameters. The molecules are approximately square planar and so, a D_{4h} effective ligand field (LF) was included in the simulations. In each case, the values for the LF parameters Dq , Ds and Dt were systematically varied to find the best fit simulation. From these ligand field plus charge transfer simulations, the most satisfactory $10Dq$, Ds and Dt values were 1.5 eV, 0.1 eV and 0.15 eV and 2.5 eV, 0.24 eV and 0.19 eV for complexes **1** and **2**, respectively (table 2).

The ground state description in the ligand field multiplet model is given by a single d^8 configuration which does not include the covalent interactions between the metal d and ligand p orbitals. To allow for bonding, the ground state can be treated within a valence bond configuration interaction (VBCI) model.^{73,74} The ground state wavefunction of a d^n system can be defined as a linear combination of the d^n configuration and the ligand to metal charge transfer, $d^{n+1}\underline{L}$ ($\underline{L}$ = ligand hole) configuration. These are separated by an energy Δ with the two components coupled by the covalent interaction given by T (the transfer integral reflecting orbital overlap). The Hamiltonian and configurations generating this ground state ($\Psi_{G,S}$) and the ligand to metal charge transfer (LMCT) excited state $\Psi_{T,S}$ are given by equations (1)-(3):

$$H = \begin{vmatrix} 0 & T \\ T & \Delta \end{vmatrix} \quad (1)$$

$$\Psi_{G,S} = \alpha_0 |3d^n\rangle + \beta_0 |3d^{n+1}\underline{L}\rangle \quad (2)$$

$$\Psi_{T,S} = \beta_0 |3d^n\rangle - \alpha_0 |3d^{n+1}\underline{L}\rangle \quad (3)$$

These equations are modified in the L-edge final state to include electronic relaxation as given by equations (4)-(7):

$$H = \begin{vmatrix} 0 & T_F \\ T_F & \Delta_F \end{vmatrix} \quad (4)$$

$$\Delta_F = \Delta + Q - U \quad (5)$$

$$\Psi_{E,S1} = \alpha |2p3d^{n+1}\rangle + \beta |2p3d^{n+2}\underline{L}\rangle \quad (6)$$

$$\Psi_{E,S2} = \beta |2p3d^{n+1}\rangle - \alpha |2p3d^{n+2}\underline{L}\rangle \quad (7)$$

where Δ_F and T_F are the charge transfer energy and the electron transfer matrix element between the two configurations in the final state and $\Psi_{E,S2}$ is the charge transfer final state. The interaction parameter T_F is approximated to be equal to the ground state parameter T . Q and U are the Cu 2p-3d and 3d-3d Coulomb interactions. Their estimated energy difference is ~ -2 eV,^{75,76} thus, Δ_F is approximately $\Delta - 2$ eV. In the case of a Cu(III) system, the value for Δ_F becomes very small and often negative (Scheme 1).^{73,76} When Δ_F is negative, the intense L_3 main peak (single peak) at ~ 930 eV is mainly a transition to the $|2p^5 3d^{10}\underline{L}\rangle$ configuration while the weak L_3 satellite peak is mostly due to a transition to the $|2p^5 3d^9\rangle$ configuration. This is the inverted bonding scheme mentioned above and is consistent with the fact that the main peak is sharp and featureless while the satellite peak exhibits multiplet structure. Using the average energy position and intensity of the L_3 multiplets at ~ 940 eV as $E_{SATELLITE}$ and

$I_{\text{SATELLITE}}$, respectively, and that of the 930 eV feature as E_{MAIN} and I_{MAIN} , equations (8) and (9) give the energy difference and intensity ratio of the main and satellite peaks.

$$E_{\text{MAIN/SATELLITE}} = \frac{1}{2} \left[\left(\Delta_F^2 + 4T_F^2 \right)^{\frac{1}{2}} \mp \Delta_F \right] \quad (8)$$

$$\frac{I_{\text{MAIN}}}{I_{\text{SATELLITE}}} = \frac{(\alpha_0\beta - \beta_0\alpha)^2}{(\alpha_0\alpha + \beta_0\beta)^2} \quad (9)$$

The inset in Figure 4B shows the relative energy shift (from the main peak) and the intensity of the shakeup transitions of the L_3 peak in **1**, **2** and **4**. The relative energy position and intensity of the shakeup peaks were simulated using the VBCI multiplet program, which determines the values for Δ ⁷⁷ and T . It should be noted that although Δ and T are not completely independent of each other, the dominant contribution in determining the energy difference between the main and satellite peaks is Δ and the relative intensity of the peaks is T . In D_{4h} symmetry there are four interaction terms, T , one for each set of symmetry orbitals: B_{1g} , A_{1g} , B_{2g} and E_g .⁷⁸ The mixing term for B_{1g} ($d_{x^2-y^2}$) is largest due to strong σ overlap of the $d_{x^2-y^2}$ orbital with the ligands. While non-zero values were used for $T(B_{1g})$, $T(E_g)$, $T(B_{2g})$ and $T(A_{1g})$, $T(B_{1g})$ was dominant and is referred to as T in the text below. Figure 5 shows the best fit multiplet simulations for complexes **1**, **2** and **4**. Table 2 gives the charge transfer parameters obtained from the simulations.⁷⁹

The L-edge spectra of **2** and **4** are qualitatively very similar. Although the L-edge spectra of both complexes are shifted up in energy by ~ 2 eV indicating a Cu(III) ground state, the small difference in the L_3 (and L_2 (Figure S1, Supporting Information)) edge energy positions [932.7 eV for **2** and ~ 932.9 eV for **4**], indicates different amounts of ligand hole character in the ground state. The satellite peak is ~ 8 eV higher in energy than the main peak for **4** compared to ~ 6 eV for **2** (Table 4) and the intensity of the satellite peak is higher in **4**. From the VBCI fits, the ground state wavefunction in **4** contains more Cu(III) character. The best fit L-edge simulations (Figure 5 and Table 2) indicate that the $|3d^8\rangle$ character in **4** is 32% while that in **2** is 26% (Cu character in the ground state is obtained from the projection method developed in ref⁷¹). Thus **2** is similar to **4** (reflecting their Cu(III) nature) but with increased ligand character in the ground state. In contrast, the L-edge spectra of **2** and **1** are very different in intensity and energy ($E_{\text{MAIN}}=932.7$ eV in **2** compared to 930.8 eV in **1**). In addition, the satellite peak is ~ 4 eV higher in energy relative to the main peak for **1**, compared to ~ 6 eV for **2** (Table 4). The intensity of the satellite peak is lower in **1** compared to **2**. The satellite peak for **2** is characterized by a double peak structure (as for Cu(III) oxides) indicating the presence of multiplet effects which are larger than for **1** (which shows a weak broad peak). In the L-edge simulations, the energy position and intensity of the satellite peak restrict the values of Δ and T and the best fit simulations for **1** give both a smaller Δ (0.24 eV compared to 0.61 eV for **2**) and a smaller T (0.9 eV compared to 1.7 eV in **2**). Using the projection method, these values give 15% Cu character in the ground state of **1** compared to 26% for **2**.⁷² The covalency values are consistent with the L-edge intensities, showing that there is an increase in electron transfer from O_2^{n-} to Cu for **1** relative to **2**.

4.2 Density Functional Theory (DFT) Calculations

4.2.1 Geometry Optimization—Broken symmetry spin-unrestricted density functional calculations were performed on models derived from the crystal structure of **1** and **2** (see Experimental Section), to correlate with the spectroscopic results to further probe their electronic structure differences. The geometry-optimized structural parameters are in good agreement with the experimental data. The calculated Cu-O and Cu-N bond distances for **1** and **2** are 1.88 Å and 1.95 Å and 1.86 Å and 1.90 Å, respectively, compared to the experimental Cu-O and Cu-N bond distances of 1.84 Å and 1.99 Å and 1.82 Å and 1.86 Å, respectively. The

first coordination bond distances are also consistent with those obtained from EXAFS results.²⁶ The calculated O-O bond distance for **2** is 1.39 Å, which is in good agreement with the experimental bond distance of 1.39 Å. While the calculated O-O distance for **1** is much longer than the crystallographic distance (1.36 Å compared to 1.22 Å),¹⁹ it has been argued that the crystallographic data underestimate the O-O distance and spectroscopic data strongly suggest that a longer bond length is appropriate.^{22,27} The Cu-O bond distances are comparable for **1** and **2** while the Cu-N bond distance for **2** is 0.05 Å shorter, indicating a stronger interaction of the diketimate ligand with the Cu relative to the pyrazole ligand-Cu interaction. The O-O bond distance for **1** is 0.03 Å shorter than for **2**, consistent with its more superoxide like character compared to the more peroxide like character for **2**.

4.2.2 Frequencies—To further correlate to the experimental assignments of **1** and **2**, frequency calculations were performed and are presented in Table 4. The O-O stretching frequencies obtained from the BP86 DFT calculations did not have appreciable mixing with other vibrational modes and hence reflect the O-O bond. The O-O stretching frequencies obtained for **1** and **2** are 1040 cm⁻¹ and 990 cm⁻¹, respectively, which are in reasonable agreement with the experimentally obtained frequencies of 1043 cm⁻¹ and 968 cm⁻¹ for complexes **1** and **2**, respectively.

4.2.3 Ground State Wavefunctions—The MO surface contour plots of the calculated singlet ground states of both **1** and **2** are presented in Figure 6. DFT calculations using BP86 give ground state descriptions that are in reasonable agreement with experimental ground state properties, in particular the singlet nature of **1**. Table 4 summarizes the compositions of selected spin-down molecular orbitals for both molecules. The Cu $d_{x^2-y^2}$ character calculated for the ψ_{LUMO}^* are 22.7% and 28.3% for **1** and **2**, respectively, consistent with the experimental values obtained from L-edges (20% and 28% in **1** and **2**, respectively). This indicates that both systems have highly covalent Cu centers. The contour plots in Figure 6 show extensive delocalization over the Cu-O₂ⁿ⁻ moiety in both complexes. The O₂ⁿ⁻ character in the β -LUMOs of **1** and **2** are 65.2 % and 54.0 %, respectively. The equatorial nitrogen atoms contribute 9.7% and 12.7% (per hole) in **1** and **2**, respectively, (the total contribution of trispyrazolyl borate and β -diketimate ligands are 17.7% and 12.3%, respectively) reflecting the greater donor strength of the bidentate β -diketimate ligand in **2**.

4.2.4 Electronic Structure Descriptions—In these approximately planar geometries the most destabilized d-orbital is $d_{x^2-y^2}$ (see Figure 2 for molecular coordinate system). The highest-lying filled molecular orbitals in the free O₂ⁿ⁻ moiety is the π^* set, which split into π_{σ}^* and π_{ν}^* upon bonding with Cu. The π_{ν}^* orbital is perpendicular to the molecular plane, hence, it does not have significant overlap with the Cu $d_{x^2-y^2}$ orbital. The in-plane π_{σ}^* orbital forms strong σ bonds with the Cu $d_{x^2-y^2}$ orbital, destabilizing it to higher energy. The NPA charge on the O₂ moiety in **2** is more negative than in **1** (Table 4, -0.74 for **2** and -0.58 for **1**), consistent with their assignments as peroxide and superoxide, respectively, which is supported by the O-O stretching frequencies and Cu K-edge data. This is also consistent with the larger Cu character in the ψ_{LUMO}^* for **2** compared to **1**.

4.2.5 K- Edge Energy Shifts—Cu K-edge and L-edge X-ray absorption spectra exhibit characteristic shifts of the pre-edge to higher energy on going from **1** to **2**, which indicate an increase in oxidation state. The K- and L-edge shift magnitudes are very similar (K-edge ~2.2 eV and L-edge ~1.9 eV). To correlate these pre-edge energy shifts with electronic structure changes on going from a Cu(II) to a Cu(III) complex, 1s→3d and 2p→3d TD-DFT calculations were performed on **1** and **2**. Note that these calculations do not include relativistic effects, so only relative energies are considered. The experimental trend in the K- pre-edge energy shift ($\Delta E_{2-1} = 2.2$ eV) is reproduced, although the TD-DFT calculated shift is 0.6 eV. The trend in

the L-edge shift ($\Delta E_{2-1} = 1.9$ eV) is also reproduced, but again the calculated energy shift is lower at 0.5 eV. Interestingly the calculated ΔE_{2-1} for both L- and K-edge are very similar (similar to the experimental shifts).

There are two potential contributions to the shifts observed in the Cu K- and L- pre-edge energies: Q_{Mol}^{Cu} the charge on the Cu atom in the molecule, and the ligand field strength.⁸⁰ An increase in Q_{Mol}^{Cu} might be expected to shift the pre-edge to higher energy due to a larger contraction of the core levels relative to the valence levels. An increase in ligand field would destabilize the ψ_{LUMO}^* and increase in the pre-edge energy. However the ligand field and Q_{Mol}^{Cu} contributions are coupled, as an increase in ligand field reflects stronger bonding between the metal and ligand orbitals which will tend to decrease Q_{Mol}^{Cu} .

To evaluate the relative contributions of ligand field and Q_{Mol}^{Cu} to the pre-edge transition energies, 1s→3d TD-DFT calculations were performed on two additional mononuclear complexes (PPh₄)₂[Cu^{II}L] and (PPh₄)[Cu^{III}L] [L= bis(methylamide) derivative of *N,N'*-*o*-phenylenebis (oxamate)]⁸¹ which differ by one electron oxidation. This pair of molecules is useful as a reference as they are both approximately square-planar, N-ligating systems similar to **1** and **2** and their experimental Cu K-edge data are available.⁶⁶ The experimental shifts in the Cu K-pre-edge energy in these complexes follow the expected trend (Cu^{III}_{pre-edge}-Cu^{II}_{pre-edge} ≈ 2 eV). The K-edge spectra of these complexes have been published and are reproduced in Figure S2 for reference.⁶⁶ Structural parameters and Mulliken atomic charges obtained from DFT calculations on [Cu^{II}L]²⁻, [Cu^{III}L]⁻ and [Cu^{III}L*]⁻ are given in Table 5. [Cu^{III}L*]⁻ corresponds to an un-relaxed ionized state of the molecule in which the geometric relaxation due to one-electron oxidation has been restricted (Scheme 2) by using the same Cu-N bond distances as in [Cu^{II}L]²⁻. The Cu-N bond distances are 1.94 Å and 1.95 Å in the optimized structure of [Cu^{II}L]²⁻ and 1.85 Å and 1.86 Å in the optimized structure of [Cu^{III}L]⁻. These distances are in excellent agreement with the X-ray crystal structure data (1.93 Å and 1.96 Å for [Cu^{II}L]²⁻ and 1.84 Å and 1.88 Å for [Cu^{III}L]⁻). In addition, the molecules are essentially square planar with no *D*_{2d} distortion. Thus, a one-electron oxidation of [Cu^{II}L]²⁻ to [Cu^{III}L]⁻ results in ~0.1 Å decrease in the ligand-Cu bond distances. The charge on Cu increases on going from [Cu^{II}L]²⁻ to [Cu^{III}L*]⁻ (1.04 to 1.15), but on going from [Cu^{III}L*]⁻ to [Cu^{III}L]⁻ the change is very small (1.15 to 1.18). The charge on the Cu is reflected in the Cu character in the β-LUMO orbital which contains 52%, 68% and 69% Cu character in [Cu^{II}L]²⁻, [Cu^{III}L*]⁻ and [Cu^{III}L]⁻, respectively. The average charge on the N atoms, which are very similar for the three complexes, are -0.76, -0.76 and -0.78 for [Cu^{II}L]²⁻, [Cu^{III}L*]⁻ and [Cu^{III}L]⁻, respectively.

TD-DFT calculations of the 1s→3d transition were performed on the optimized structures obtained from the DFT calculations using ORCA.^{56,57} This ensures that the ligand fields between [Cu^{II}L]²⁻ and [Cu^{III}L*]⁻ are similar. Additionally, on going from [Cu^{III}L*]⁻ to [Cu^{III}L]⁻ where the molecule has now been geometry optimized to allow for structural relaxation, the charge on Cu remains the same (Table 5). Thus, the 1s→3d transition energies obtained from the TD-DFT calculations should predominantly reflect the effect of a change in charge on Cu on going from [Cu^{II}L]²⁻ to [Cu^{III}L*]⁻ and a change in ligand field on going from [Cu^{III}L*]⁻ to [Cu^{III}L]⁻. The transition energies obtained from the 1s→3d TD-DFT calculations are given in Table 5. The trend observed for the experimental transition energies is reproduced by the TD-DFT calculations and the shift due to one-electron oxidation is ~1 eV (compared to ~2 eV for the experimental data). However, the change in 1s→3d transition energy on going from [Cu^{II}L]²⁻ to [Cu^{III}L*]⁻ is only ~0.2 eV while the change on going from [Cu^{III}L*]⁻ to

[Cu^{III}L]⁻ is ~0.8 eV. Thus, although most of the Q_{Mol}^{Cu} increase occurs on going from [Cu^{II}L]²⁻ to [Cu^{III}L*]⁻ (11%) there is only a very small shift in calculated K- pre-edge energy.

However, while there is almost no change in Q_{Mol}^{Cu} (~1%) on going from [Cu^{III}L*]⁻ to

[Cu^{III}L]⁺, there is a significant change in the pre-edge energy. This indicates that the contribution of Q_{Mol}^{Cu} to the pre-edge transition energy is, in fact, very small and that these energy shifts are dominated by changes in ligand field. This is consistent with the observation that similar shifts are observed in L- and K- pre-edge transition energies between **1** and **2**, thus, the change in Q_{Mol}^{Cu} leads to similar energy shifts in the Cu 1s, 2p and 3d orbitals and the pre-edge shift observed is predominantly due to ligand field. In **1** the N containing ligand system is tris-pyrazolyl borate, which forms two fairly weak Cu-N bonds in the equatorial position at ~2 Å (a weak ~2.25 Å Cu-N is also present).⁸² In contrast, the partial negative charge on the nitrogens of the β -diketiminato ligand leads to the formation of strong Cu-N bonds (at ~1.86 Å) in **2**, increasing the ligand field and destabilizing the $d_{x^2-y^2}$ orbital relative to that in **1**. This is consistent with DFT calculations which indicate larger nitrogen character (18% per-hole) in **2** relative to **1** (12% per-hole). This is also consistent with the [LCu-thiolate] study of Randall *et al.*⁸⁰ which showed, using a combination of magnetic circular dichroism (MCD) and XAS studies, that the β -diketiminato ligand interacts more strongly with Cu resulting in larger destabilization of the $d_{x^2-y^2}$ orbital relative to the trispyrazolylborate ligand. This increase in ligand field leads to the large shift observed in the K pre-edge of **2** relative to **1**.

5. Discussion

5.1 Nature of Cu-O₂ bonds

Resonance Raman spectroscopic studies and theoretical calculations have been performed on complexes **1** and **2** which indicate their respective superoxide vs peroxide nature.^{22,25-27, 83,84} In this study, Cu K- and L-edge data on **1** and **2** combined with the results obtained from VBCI analysis of the L-edge spectra are used to experimentally probe differences in the Cu-O₂ⁿ⁻ bonding and to evaluate the nature of the Cu-O₂ⁿ⁻ bond in **1** and **2**. Quantitating the total integrated intensities under the L-edge peaks (Figure 4A) indicates that both complexes are very covalent and that **1** has a ground state with 20% Cu character while for **2** the Cu character is 28%. Further, the L-edge of **2** has a larger gap between the main and satellite peaks and higher intensity of the satellite features at ~ 935-940 eV, which also exhibit more multiplet structure. VBCI simulations of these L-edge spectra reproduce the strongly covalent nature of the ground states with more d⁸ Cu(III) character in **2**. In the VBCI framework, two factors contribute to the covalent mixing of the d⁸ Cu(III) ground state with the charge transfer excited state: *i*) a small Δ term where the two interacting states are close in energy and *ii*) a large T term for the interaction (L-M overlap) between them. The Δ and T values for **1** and **2** obtained from the best fit VBCI simulations are 0.24 eV and 0.9 eV and 0.61 eV and 1.7 eV, respectively. The higher value of T for **2** more than compensates for its larger Δ , leading to a net increase in the amount of Cu character in the ground state wavefunction relative to **1**.

DFT calculations are consistent with previous theoretical studies²⁷ and support the experimental results and analysis. The experimental trends in the O-O stretching frequencies of 1043 cm⁻¹ and 948 cm⁻¹ for **1** and **2** are reproduced by the calculations (1040 cm⁻¹ for **1** and 990 cm⁻¹ for **2**) and support the electronic structure description of **1** and **2** as superoxide and peroxide copper complexes, respectively. The experimental trend in the Cu character in the ψ_{LUMO}^* is also reasonably reproduced. The differences in the ligand character in the ψ_{LUMO}^* indicate that the planar ring system of the β -diketiminato and anionic charge localization on the N's lead to a very strong bonding interaction with Cu and significant charge donation from the β -diketiminato, stabilizing the Cu(III) state. The strong interaction of β -diketiminato with Cu relative to tris(pyrazolyl)hydroborate was described in a spectroscopic study by Randall *et al.*⁸⁰ in which it was demonstrated that the increased donation of the β -diketiminato ligand weakens the Cu-thiolate bond relative to the tris(pyrazolyl)hydroborate ligand system. This result was invoked in a theoretical study on derivatives of **1** and **2** by Cramer *et al.*²⁷ which indicate that an electron rich metal tends to form a peroxide species.

In the Cu-thiolate study by Randall *et al.*,⁸⁰ although the thiolate character in the ψ_{SOMO}^* changes significantly, the Cu character remains very similar in both complexes. In contrast, in the Cu-O₂ⁿ⁻ systems the interaction between the π^*_σ orbital on O₂ⁿ⁻ and the 3d_{x²-y²} orbital on Cu leads to a very covalent two hole system, which results in Cu(II)-superoxide or Cu(III)-peroxide character depending on the relative contributions of Cu and O to the ψ_{LUMO}^* . It is important to note that in contrast to the Cu^{II}-thiolate systems, the Cu character in **1** and **2** are different. This difference arises from the presence of additional electron repulsion on going from a d⁹ to a d⁸ system, which localizes Cu character in the ψ_{LUMO}^* .

This difference in the composition of the ψ_{LUMO}^* indicates that the ligand environment regulates the O₂ⁿ⁻ character in the ground state. The amount of O₂ⁿ⁻ character in the ψ_{LUMO}^* is larger in **1** (65% π^*_σ) compared to **2** (54% π^*_σ). This is critical in terms of reactivity in PHM and D β M as it indicates that the frontier molecular orbital (FMO) of a superoxide-like species would be activated towards H-atom abstraction.¹¹ The ligand system of the Cu_M site in PHM (2 N(His), 1 S(Met) and 1(H₂O)) is similar in ligand field to the trispyrazolyl ligation in **1**.^{10,17} This is consistent with various experimental and theoretical studies on PHM which implicate (and possibly observe) the formation of a [Cu^{II}-O₂⁻] intermediate which is tuned towards substrate hydroxylation.^{3,11,18} Thus, this study provides insight into the ligand environment contribution to the formation of a [Cu^{II}-O₂⁻] intermediate in PHM (and D β M) and in tuning its reactivity.

5.2 Contributions to Pre-edge Energy Shifts

L-edge intensity is a direct probe of the total metal character in the β -LUMO and thus directly reflects the charge on the metal atom in the molecule (Q_{Mol}^M).⁸⁵ It has been shown by X-ray photoelectron spectroscopy that changes in Q_{Mol}^M result in large shifts in the ionization energies, referred to as chemical shifts, which reflect the formal oxidation state of the atom in the molecule. This might indicate that the L-pre-edge energy should increase with increase in the relative L-edge intensity. Figure 7A shows a comparison of the Cu L₃ pre-edges of [Cu(TMPA)(OH₂)](ClO₄)₂ (**3**, **2** and the blue copper site in plastocyanin. The normalized L-edge intensities of **3**, **2**, and plastocyanin are 55%, 56% (28% per hole) and 42%, respectively. The effective charge on copper is quite different between **3** and plastocyanin, yet the pre-edge energy positions for both occur at 930.8 eV. In contrast, the charge on copper is the same for **2** and **3**, while the pre-edge for **2** is at 932.7 eV, ~ 2 eV higher than for **3**. Thus the L-edge energy positions do not directly reflect Q_{Mol}^{Cu} . The calculations on [Cu^{II}L]²⁻, [Cu^{III}L*]⁻ and [Cu^{III}L]⁻ presented in section 4.2.5 also indicate that there is very little effect on the edge energy due to change in charge on the copper and the dominant contribution to the edge shift is from the increased ligand field at the Cu(III) in the complex.

The effect of change in charge on an atom in a molecule (ΔQ_{Mol}^M) on the 2p and 3d orbitals has been modeled.^{86,87} This ΔQ_{Mol}^M modeling was extended in this study to obtain the relative change in 1s and 2p core and 3d valence orbital energies in a copper atom due to ΔQ_{Mol}^{Cu} . The correlation of the core(1s):core(2p) orbital energies was found to be ~1:1 while the core:valence correlation is ~0.9:1 (Figure S3). These results are consistent with XPS data, which show that over a series of compounds with different Q_{Mol}^M 's (due to differences in formal oxidation state), the chemical shifts observed in the valence and core levels are approximately the same. Since metal K- and L- pre-edges probe transitions between two bound states, the energy shift due to change in Q_{Mol}^M is small.^{88,89} Thus, the energy shifts associated with pre-edges reflect contributions from the ligand field. Figure 7B shows a comparison of the Cu K-

edges of **2** and **3**. The K pre-edge energy shift is ~ 2 eV which is similar to the L- pre-edge energy shift (Figure 7A). Since the ligand field dominantly affects the valence orbitals involved in bonding, the shifts in the Cu K- and L-edge are necessarily very similar (within resolution).

5.3 Electronic Structure of Cu^{III} Compounds

Cu(III) complexes are important chemical oxidants, implicated as intermediates in oxidative processes and comprise an important class of superconductors.^{66,73,78,90} In recent years a number of Cu(III) complexes have been characterized⁹¹⁻⁹³ and crystal structures and EXAFS data on these indicate that the first shell Cu(III)-L distance is 0.1 Å shorter than in similar Cu(II) complexes. In an extensive X-ray absorption Cu K-edge study, DuBois. *et al.*⁶⁶ have shown that the Cu K-edge of Cu(III) complexes look dramatically different from those of Cu(II) complexes and have assigned the ~ 2 eV pre-edge shift (~ 8979 eV to ~ 8981 eV) as a signature of a unit increase in oxidation state. It is shown in the present study that this shift in the pre-edge energy position for both K- and L-edges is, in fact, dominated by ligand field contributions. The L-edge intensity of **2**, a Cu(III) complex, is very similar to that of normal Cu(II) complexes (Figure 7A), indicating that their Q_{Mol}^{Cu} 's are very similar. This similarity in L-edge intensity combined with the 0.1 Å shortening of Cu-L bonds, indicate that Cu(III) complexes have very strong covalent bonds. Hence, the charge built up by the one-electron oxidation of a Cu(II) to a Cu(III) species is neutralized by extensive charge donation by the ligand framework to the metal. This reflects Pauling's electroneutrality principle.

In summary, the electronic structures of two mononuclear LCuO₂ systems, **1** and **2** have been evaluated using Cu K- and L-edge XAS coupled with calculations. The XAS data, particularly the L-edge intensities, clearly demonstrate the Cu(II)-O₂⁻ and Cu(III)-O₂²⁻ natures of **1** and **2**, respectively. These differences reflect the difference in donor interactions of L with Cu (greater in **2**) coupled with the increased electron repulsion in these two-hole systems. Ligand field and Q_{Mol}^{Cu} contributions to Cu K- and L- pre-edge shifts have been evaluated using a DFT and TD-DFT calculations and through correlation to XPS data. It is found that for bound state transitions, the pre-edge energy shift is dominated by the ligand field and is less affected by a change in Q_{Mol}^{Cu} . Finally, it is shown that Cu(III) compounds can have similar Q_{Mol}^{Cu} 's to those of Cu(II) complexes due to increased donor interaction with the ligand to compensate for the increased charge on the metal center.

Supplementary Material

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Abbreviations

XAS, X-ray absorption spectroscopy
 VBCI, Valence bond configuration interaction
 DFT, Density functional theory
 Q_{Mol}^M , Charge on the absorbing metal (M) in a molecule

TD-DFT, Time-dependent density functional theory
UHV, Ultra high vacuum
LMCT, Ligand to metal charge transfer
 β -LUMO, Spin-down lowest unoccupied molecular orbital
FMO, Frontier molecular orbital
LF, Ligand field
EXAFS, Extended X-ray absorption fine structure
NPA, Natural population analysis
MPA, Mulliken population analysis

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Figure 1. The pre-catalytic active site of peptidylglycine *R*-hydroxylating monooxygenase (PHM) showing the binuclear Cu site separated by $\sim 11 \text{ \AA}$. The O_2 is bound asymmetrically to the Cu_M site.

Figure 2.

The crystal structures of **1(A)** and **2(B)**. The *i*Pr and *t*Bu groups on the pyrazole ring and β -diketiminate ligand systems have been removed for clarity. Refer to text for bond length parameters.

Figure 3. The normalized Cu K-edge XAS spectra of $[^1\text{LCu}(\text{O}_2)]$ **1** (—) and $[^2\text{LCu}(\text{O}_2)]$ **2** (—). Inset shows the expanded pre-edge region ($1s \rightarrow 3d$ transition) indicating a ~2 eV shift.

Figure 4.

(A). The normalized Cu L-edge XAS spectra of [¹LCu(O₂)] **1** (→) and [²LCu(O₂)] **2** (→) and *D*_{4h} [CuCl₄]²⁻ (→). The intense peaks at ~ 930 eV and ~ 950 eV represent the L₃ edge (2p_{3/2} → 3d transition) and L₂ edge (2p_{1/2} → 3d transition). (B). The expanded Cu L₃-edge X-ray absorption spectra of [¹LCu(O₂)] **1** (→) and [²LCu(O₂)] **2** (→) and La₂Li_{1/2}Cu_{1/2}O₄ **4** (→). Inset displays the expanded shakeup region (satellite peak) showing the relative shift in the satellite peak from the main peak (main peak energy positions have been rescaled to 0 eV).

Figure 5. L-edge multiplet simulations. The VBCI simulations of $[^1\text{LCu}(\text{O}_2)]$ (1), $[^2\text{LCu}(\text{O}_2)]$ (2) and $\text{La}_2\text{Li}_{1/2}\text{Cu}_{1/2}\text{O}_4$ (4), are shown in panels (A), (B) and (C), respectively. Data are shown in black and simulations are shown in red. The red lines represent the stick spectra and correspond to the transitions with intensity. The stick spectra have been convoluted with a pseudo-Voigt shape to simulate experimental spectra.

Figure 6. Molecular orbital contour plots of $[^1\text{LCu}(\text{O}_2)]$ **1** and $[^2\text{LCu}(\text{O}_2)]$ **2** shown in panels (A) and (B), respectively. The contour plots have been generated in MOLDEN. The Mulliken population of ψ_{LUMO}^* is shown next to the relevant atom(s). L denotes trispyrazolyl borate and β -diketiminato in **1** and **2**, respectively.

Figure 7.

(A) The normalized Cu L₃-edge spectra of [Cu^{II}(TMPA)(OH₂)](ClO₄)₂ **3** (—), plastocyanin (—) and [2LCu(O₂)] **2** (—). (B) The normalized Cu K-edge spectra of [Cu^{II}(TMPA)(OH₂)](ClO₄)₂ **3** (—) and [2LCu(O₂)] **2** (—). Inset shows the expanded pre-edge region (1s → 3d transition)

Scheme 1.

Schematic energy diagram of the charge transfer interaction in the ground and excited states of a $3d^n$ system covalently interacting with a ligand $2p/3p$ orbital. Panel (A) shows the ground state configuration interaction. Panel (B) and (C) show the excited state CI mixing with positive and negative charge transfer energy, respectively.

Scheme 2.

A schematic representation of the changes in the 1s, 2p and 3d orbital energies upon one electron oxidation of $[\text{Cu}^{\text{II}}\text{L}]^{2-}$ to $[\text{Cu}^{\text{III}}\text{L}^*]^-$ and to $[\text{Cu}^{\text{III}}\text{L}]^-$. The formation of $[\text{Cu}^{\text{III}}\text{L}^*]^-$ involves a change in Z_{eff} while formation of $[\text{Cu}^{\text{III}}\text{L}]^-$ involves a change in both ligand field and Z_{eff} , indicating that ligand field effects have a dominant contribution to the energy shift and $E^1 \approx E^2 < E^3$. [L.F = ligand field, np = 2p(O)]

Table 1
Cu K- and L-edge X-ray Absorption Edge Energies (eV) and Cu Character in ψ_{LUMO}^*

	Cu K-edge ^a			Cu L-edge ^b			Cu character in ψ_{LUMO}^* (per-hole)
	1s→3d	1s→4p + shakedown	L ₃ edge	2p→3d	L ₂ edge		
[Cu(O ₂){HB(3-Ad-5-Prpz) ₃ }] (1)	8978.6	8988.3 ^d	930.8		950.7		20%
[Cu(O ₂)(β -diketimate)] (2)	8980.7	8986.5	932.7		952.7		28%
(C ₄ H ₈ N ₃ O ₂)[CuCl ₄] (<i>D_{4h}</i>) ^e	8978.6	8986.8	931.0		951.0		61%

^aEnergy resolution ~1 eV.

^bEnergy resolution ~0.1 eV.

^c**1** & **2** are two-hole systems (see text for detail).

^dThe energy is determined from second derivative intensity as the shakedown feature is less pronounced in Cu^{II} systems.

^eCreatinium tetrachloro cuprate(II).

Table 2
Parameters Used in Multiplet Simulations and Ground State Description of ψ_{LUMO}^*

Crystal Field Parameters (eV)			Δ	Ligand Field Parameters (eV) ^a			T _{B2}	3d ⁿ ⟩ Character in ψ_{LUMO}^*
10Dq	Ds	Dt		T _{B1} ^b	T _{A1}	T _{A1}		
1	1.5	0.1	0.15	0.9	0.35	0.2	0.15	15%
2	2.5	0.24	0.19	1.7	0.2	0.1	0.1	26%
4	6.0	0.3	0.4 ^d	3.5	1.0	0.2	0.1	32%

^aThe ligand field simulations were performed under *D*4*h* symmetry (T_{B1} = T_X²-y² etc).

^bThe dominant contribution in determining the intensity of satellite peak was from T_{B1}.

^cDetermined from the projection method.

^dDt is used to obtain the correct crystal field description.

Table 3
Energy and Intensity Ratios of Main and Satellite Peaks of the L₃ Edge

	2p_{3/2} → 3d (L₃ edge)		ΔE (eV)^a
	Main Peak (eV)	Satellite Peak (eV)	
1	930.8	934.7	3.9
2	932.7	938.8	6.1
4	932.9	940.2	8.3

^aThe satellite peak position was determined at the average energy of the multiplet structure.

Table 4

Selected Parameters from DFT Calculations

	Bond Distance (Å)			O-O Stretching Frequency (cm ⁻¹)	β -LUMO Composition				Natural Charge		
	Cu-O	Cu-N	O-O		Cu	O ^a	N ^a	L ^b	Cu	O	N
1	1.88	1.95	1.36	1040	22.7	65.2	9.7	2.4	1.22	-0.58	-1.20
2	1.86	1.90	1.39	990	28.3	54.0	12.7	5.0	1.21	-0.74	-1.30

^a β -LUMO Composition and Natural charge represent the sum total on the two O and N atoms.

^b L represents the tripyrazolyl borate and diketiminate ligand system in **1** and **2**, respectively.

Table 5
Selected DFT Parameters and Comparison of Cu K-edge and TD-DFT Transition Energies

	DFT (Gaussian)		1s→3d Transition (eV)		
	Bond Distance (Å)		TD-DFT (ORCA) ^a		
	Cu-N ₁ (N ₂)	Cu	Mulliken Charge	TZVP	6-311G*
[Cu ^{II} L] ²⁻	1.94(1.95)	1.04	-0.71(-0.82)	8749.2	8748.2
[Cu ^{III} L*] ⁻	1.94(1.95) ^b	1.15	-0.71(-0.82)	8749.4	8748.4
[Cu ^{III} L] ⁻	1.85(1.86)	1.18	-0.74(-0.83)	8750.1	8749.2

^aDFT underestimates the core binding energy, the energies are reported for relative comparison.

^bThe bond distances in [Cu^{III}L*]⁻ (single-point calculation) are identical to the [Cu^{II}L]²⁻.