Spectroscopic and Electronic Structure Studies of the Diamagnetic Side-On Cu\textsuperscript{II}-Superoxo Complex 
Cu(O\textsubscript{2})(HB(3-R-5-Prpz)\textsubscript{3}]: Antiferromagnetic Coupling versus Covalent Delocalization

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Abstract: Magnetic, vibrational, and optical techniques are combined with density functional calculations to elucidate the electronic structure of the diamagnetic mononuclear side-on Cu\textsuperscript{II}-superoxo complex. The electronic nature of its lowest singlet/triplet states and the ground-state diamagnetism are explored. The triplet state is found to involve the interaction between the Cu xy and the superoxide \(\pi^*\) orbitals, which are orthogonal to each other. The singlet ground state involves the interaction between the Cu xy and the in-plane superoxide \(\pi^*\) orbitals, which have a large overlap and thus strong bonding. The ground-state singlet/triplet states are therefore fundamentally different in orbital origin and not appropriately described by an exchange model. The ground-state singlet is highly delocalized with no spin polarization.

1. Introduction

Oxygen activation by copper proteins is a very important process in biology.\textsuperscript{1,2} Reactive Cu-oxygen intermediates play a central role in many biological enzymatic pathways and homogeneous catalytic cycles.\textsuperscript{3–7} Mononuclear Cu\textsuperscript{II}-superoxo species are likely involved in the chemistry at several Cu protein active sites, such as Cu/Zn superoxide dismutase,\textsuperscript{8} dopamine \(\beta\)-monooxygenase,\textsuperscript{2} peptidylglycine \(\alpha\)-hydroxylating monoxygenase,\textsuperscript{9,10} and copper amine oxidase.\textsuperscript{11} In synthetic copper/oxygen model chemistry, the mononuclear Cu\textsuperscript{II}-superoxo species is believed to be the precursor to oxygen binding and activation in peroxy/oxo bridged binuclear Cu complexes.\textsuperscript{5,6,12,13} A number of mononuclear Cu\textsuperscript{II}-superoxo complexes have been synthesized and are EPR silent, indicating a diamagnetic ground state.\textsuperscript{14–21} The diamagnetic property of the Cu\textsuperscript{II}-superoxo complex has been generally ascribed to the antiferromagnetic coupling between the spins on the Cu\textsuperscript{II} atom and the superoxide radical.\textsuperscript{14,19}

The only structurally characterized Cu\textsuperscript{II}-superoxo complex, Cu(O\textsubscript{2})(HB(3-Bu-5-Prpz)\textsubscript{3}) (referred to as L3CuO\textsubscript{2}, HB(3-Bu-5-Prpz)\textsubscript{3} = hydrotris(3-tert-butyl-5-isopropyl-1-pyrazolyl)borate), has the superoxide ligand bound in a side-on mode (Figure 1).\textsuperscript{18,21} The complex has an O–O bond length of \(\sim 1.22\) Å and an O–O vibrational frequency of 1112 cm\(^{-1}\) in its IR spectrum, which shifts to 1060 cm\(^{-1}\) in the 18-oxygen isotope labeled sample, consistent with its description as a superoxide complex.\textsuperscript{22} The +2 oxidation state of the Cu atom in the Cu\textsuperscript{II} complex.

\begin{thebibliography}{99}


(12) Blackman, A. G.; Tolman, W. B. In Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations; Meunier, B., Ed.; Springer-Verlag: Berlin, 2000, p 179.


(21) There was a misassigned mononuclear end-on Cu\textsuperscript{II}-superoxo complex which was later reassigned as a mononuclear Cu\textsuperscript{II}-hydroxo complex. See: Berreau, W. S.; Knowles, P. F. J. Am. Chem. Soc. 1991, 113, 7744.


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superoxo complex is confirmed by its Cu K-edge X-ray absorption spectrum, which shows a small preedge feature at ~8979 eV, characteristic of a CuII center.23,24

In this study, we combine magnetic and spectroscopic characterizations with density functional calculations to elucidate the electronic structure of this side-on CuII-superoxo complex. The nature of the lowest singlet and triplet states of the complex was investigated, and a detailed description of the ground-state diamagnetism is developed to obtain insight into the magnetic properties and bonding interactions between CuII and the superoxide ligand. Over the course of this study, it was determined that there is some contamination of a dimeric L3CuII-superoxo species, which obscure the CuII-superoxo spectral features, an analogous Cu(O2)[HB(3-Ad-5-Prpz)] complex (referred to as L10CuO2, HB(3-Ad-5-Prpz)) was synthesized. The adamantyl side chain on the pyrazole ring was removed by filtration with Celite. The filtrate was evaporated to dryness. The result solid was recrystallized from ether/CH2Cl2 at ~30 °C to afford a colorless powder. yield 0.26 g (58%). Anal. Calcd for L10CuCl (0.45 g, 0.75 mmol) 26 was dissolved in 40 mL of CH2Cl2 and 10 mL of DMF. After being cooled at ~50 °C, an excess amount of KO2 solid was added to this solution. The color of this solution turned gradually to pale yellow from brownish red. After the reduction reaction was completed, the remaining KO2 was removed by filtration with Celite. The filtrate was evaporated to dryness. The resultant solid was recrystallized from DMF at ~30 °C to afford a colorless powder. Yield 0.27 g (56%). Anal. Calcd for C30H52N6BCuO2: C, 66.20; H, 8.13; N, 9.55; Found: C, 65.87; H, 8.19; N, 9.53. Uv–vis (CH2Cl2, 77 K, 363.8 nm ext): 308 nm (ε, 300 M−1 cm−1), 700 nm (sh, 40), 975 nm (20). FTIR (cm−1): ν(C=O) 1660. 1H NMR (δ/ppm, CD2Cl2, 500 MHz, 20 °C): 1.22 (d, J = 6.9 Hz, 18H, CHMe2), 1.79 (m, 18H, Ad-Hδ), 2.09 (br, 9H, Ad-Hβ), 2.82 (s, 3H, HCONMe), 3.44 (septet, J = 6.9 Hz, 3H, CHMe2), 5.82 (s, 3H, CH2), 7.96 (s, 1H, HCONMe).

L10CuCl2. L10CuCl2 (0.40 g, 0.75 mmol)26 was dissolved in 50 mL of CH2Cl2 and 10 mL of DMF. After being cooled at ~50 °C, an excess amount of KO2 solid was added to this solution. The color of this solution turned gradually to pale yellow from brownish red. After the reduction reaction was completed, the remaining KO2 was removed by filtration with Celite. The filtrate was evaporated to dryness. The resultant solid was recrystallized from ether/CH2Cl2 at ~30 °C to afford a colorless powder. Yield 0.26 g (58%). Anal. Calcd for L10CuCl2 (DMF)-CH2Cl2, C33H59N7BCuO2Cl: C, 61.52; H, 9.23; N, 15.22. Found: C, 61.10; H, 9.11; N, 15.38. FTIR (cm−1, KBr): ν(C=O) 2530, ν(CO) 1661. 1H NMR (δ/ppm, CD2Cl2, 400 MHz, 25 °C): 1.22 (d, J = 6.7 Hz, 18H, CHMe2), 1.35 (s, 27H, CHMe2), 2.78 (s, 3H, HCONMe), 2.95 (s, 3H, HCONMe), 3.58 (m, J = 6.7 Hz, 3H, CHMe2), 5.84 (s, 3H, pZ-H), 8.02 (s, 1H, HCONMe).

(24) Note an alternative description of CuII-superoxo is the iso-electronic CuIII-superoxo description, which, however, would have very different electronic spectroscopic properties, that is, different d−d transition energies due to the +3 oxidation state of Cu and a much lower O−O vibrational frequency.
(26) The detailed synthetic methods and their properties will be described in a separate paper.

L3CuO2. L3Cu(DMF) (0.30 g) was dissolved in 10 mL of CH3Cl2. After this solution was cooled at ~78 °C, dioxygen was introduced to this tube. After being recrystallized at ~78 °C overnight, the reddish brown powder was collected by filtration. Anal. Calcd for C48.5H71N6BCuO2: C, 69.74; H, 8.69; N, 13.93. Found: C, 69.39; H, 8.85; N, 13.39. Uv−vis (CH2Cl2, 23 °C): 352 nm (ε, 2300 M−1 cm−1), 510 nm (sh, 230), 660 nm (90). FTIR (cm−1, KBr): ν(C=O) 2564, ν(O−O) 1112 (ν(Cu−O−O) 1062), ν(Cu−O) 550 (ν(Cu−O−O) 534). Resonance Raman (cm−1, CH2Cl2, 77 K, 363.8 nm ext): 308 (ν(C=O), 2ν(C=O) 1097 (2ν(C−O) 1050). (406.7 nm ext): ν(C=O) 554 (ν(C−O) 534). 1H NMR (δ/ppm, CD2Cl2, 400 MHz, ~40 °C): 1.19 (d, J = 6.4 Hz, 18H, CHMe2), 1.66 (s, 27H, CHMe2), 3.36 (m, J = 6.4 Hz, 3H, CHMe2), 6.19 (s, 3H, pZ-H).

2. Experimental Section

Materials and Synthesis. All reagents were of the highest grade commercially available and were used without further purification unless otherwise noted. Dichloromethane, diethyl ether, and toluene were carefully purified by distillation under argon atmosphere from P2O5 and sodium/benzophenone ketyl, respectively. Preparation and handling of air-sensitive materials were performed under an argon atmosphere using standard Schlenk techniques or a glovebox.

L3CuCl2(DMF), L3CuCl (0.45 g, 0.75 mmol)26 was dissolved in 40 mL of CH3Cl2 and 10 mL of DMF. After the mixture was cooled at ~50 °C, an excess amount of KO2 solid was added to this solution. The color of this solution turned gradually to pale yellow from brownish red. After the reduction reaction was completed, the remaining KO2 was removed by filtration with Celite. The filtrate was evaporated to dryness. The resultant solid was recrystallized from DMF at ~30 °C to afford a colorless powder. Yield 0.27 g (56%). Anal. Calcd for C61.52; H, 9.23; N, 15.22. Found: C, 61.10; H, 9.11; N, 15.38. FTIR (cm−1, KBr): ν(C=O) 2530, ν(CO) 1661. 1H NMR (δ/ppm, DCON(CD3), 400 MHz, 25 °C): 1.22 (d, J = 6.7 Hz, 18H, CHMe2), 1.35 (s, 27H, CHMe2), 2.78 (s, 3H, HCONMe), 2.95 (s, 3H, HCONMe), 3.58 (m, J = 6.7 Hz, 3H, CHMe2), 5.84 (s, 3H, pZ-H), 8.02 (s, 1H, HCONMe).

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Figure 1. Crystal structure of Cu(O2)[HB(3-But-5-Prpz)]. The CuO2 plane is defined as xz with the x-axis bisecting the O−Cu−O angle.
Electron magnetic moment and spectroscopy. 3.1.1. Magnetoochemistry. Figure 2 gives the temperature dependence of the effective magnetic moment $\mu_{\text{eff}}$ of L3Cu2O3 taken on the same

Instruments ST-135. The samples contained in NMR tubes were immersed in a liquid nitrogen finger dewar. Raman peak intensities were referenced to the CH2 Cl2 solvent peaks for excitation profiles. IR and far-IR spectra were recorded in a solid KBr disk and a solid CsI disk, respectively, on a JASCO-550 spectrometer. Elemental analyses were determined at an analytical facility at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology, and the Chemical Analysis Center of the University of Tsukuba.

Electronic Structure Calculations. Density functional theory (DFT) calculations were performed on a PC cluster and a SGI Origin 2000 workstation. ADF 20127 was used for ground-state and excited-state calculations. Analysis Center of the University of Tsukuba.

Figure 2. SQUID measured effective magnetic moment $\mu_{\text{eff}}$ (B.M. ÷ Bohr magneton) of L3Cu2O3. Lines are the simulated curves assuming the S/T energy splitting ($E_{S1} - E_{T1}$) = 1800, 1600, 1500, 1400, or 1200 cm$^{-1}$.

Figure 3. (A) UV/vis absorption spectrum of L10CuO2 in CH2Cl2 at ~70 °C (solid line) with Gaussian resolved individual transitions (dashed lines). Overlaid is the rR profile of the 1043 cm$^{-1}$ vibrational mode of L10CuO2 (○). (B) Variable temperature near-IR null absorption spectra of L10CuO2; Vibrational overtones of the nulling agent are labeled as "*".

batch of crystalline solid used for crystal structure determination.18 The purity of the sample is confirmed by the crystallographic characterization and elemental analysis (see Experimental Section). The $\mu_{\text{eff}}$ is almost zero at low temperature (<150 K), confirming the diamagnetic singlet ground state ($S = 0$) of the molecule ($\mu_{\text{eff}}$ ≈ 2.83 μB for the $S = 1$ state). The $\mu_{\text{eff}}$ deviates slightly from zero at higher temperatures, and this deviation is not present in control experiments on pure diamagnetic materials, suggesting the presence of a low-lying triplet excited state ($S = 1$) with a small thermal population. The magnetic properties of L3Cu2O3 could be analyzed using the Bleaney and Bowers equation $\chi = (2N^2\beta^2/kT)[1 + \exp(-\Delta_S/kT)]$, where $\Delta_S$ is the singlet/triplet (S/T) energy splitting ($\Delta_S = E_{S1} - E_{T1}$), and $\mu_{\text{eff}} = (3y/kT\beta^2)^{1/2}$. The best fit to the data estimates a low-lying excited triplet state at 1500 ± 300 cm$^{-1}$ above the singlet ground state (Figure 2).

3.1.2. Electronic Absorption. The previously reported L3Cu2O3 solution absorption spectrum shows a band at ~350 nm (~28 800 cm$^{-1}$) with $\epsilon$ ≈ 2330 M$^{-1}$ cm$^{-1}$ (Figure S1A).18 This absorption band is in fact from a dimeric L3Cu(II)Cu(II) L3 component, which has an intense charge-transfer absorption band at ~350 nm with $\epsilon$ > 20 000 M$^{-1}$ cm$^{-1}$ obscuring the Cu(II)superoxide spectral features.25 The presence of this dimer component was identified by the rR spectra on the solution samples of L3Cu2O3 excited at 363.8 nm (~27 500 cm$^{-1}$), which show an intense Cu–Cu vibrational mode at 308 cm$^{-1}$, characteristic of the side-on peroxo dimer (Figure S1B).35 This component is not present in the solid sample used for the magnetic susceptibility measurements, which came from the crystalline solid used for crystallographic characterization.18 To avoid this dimer component in solution, the analogous complex Cu(O2)[HB(3-Ad-5-Ppz)] (L10CuO2) was synthesized. Its absorption spectrum indicates that the much bulkier adamantyl ligand prevents dimerization in solution.

The UV/vis solution absorption spectrum of L10CuO2 in CH2Cl2 is presented in Figure 3A.36 No intense absorption band is present, and four weak transitions are observed at 12 200, 14 100, 15 000, and 18 800 cm$^{-1}$, respectively.

14 300, 22 100, and 26 100 cm\(^{-1}\) with extinction coefficients all <400 M\(^{-1}\) cm\(^{-1}\). These bands are assigned as Cu\(^{II}\) d–d transitions on the basis of their low extinction coefficients. Their energies are similar to those of ligand field transitions of square pyramidal Cu\(^{II}\) complexes.\(^{(37)}\) The onset of an intense absorption band occurs at energies >30 000 cm\(^{-1}\).

Calculations predicted the presence of an additional low-lying singlet excited state (<10 000 cm\(^{-1}\), see section 3.2.1). Therefore, the absorption measurement of L10CuO\(_2\) was extended into the near-IR region. A null sample was used to avoid the strong vibrational overtone absorption of solvents. An electronic transition is observed at 4200 cm\(^{-1}\) with \(\epsilon \approx 200\) M\(^{-1}\) cm\(^{-1}\) (Figure 3B).\(^{(38)}\) This low energy transition is not present in the thermodecomposed product, which is the Cu\(^{II}\) complex resulting from loss of the coordinated superoxide as dioxygen. This transition is also not observed for the bis(\(\mu\)-OH) bridged dimeric L1Cu\(^{II}\)(OH)\(_2\)Cu\(^{II}\)L1 complex (L1 = [HB(3,5-\(\text{Prpz}\))\(\_3\)], hydrotris-(3,5-diisopropyl-1-pyrazolyl)borate), which has a similar five-coordinate Cu\(^{II}\) with the hydrotris(pyrazolyl)borate ligand (Figure S4).\(^{(39)}\) This excludes the possibility of this transition being a broad vibrational overtone envelope of the hydrotris(pyrazolyl)borate ligand and indicates it is an electronic transition associated with the superoxide complex. The electronic nature of this transition is further supported by the broadening in its bandwidth and the decrease in amplitude at high temperature due to the Franck–Condor factor in absorption\(^{(40)}\) and the decreased excited-state lifetime from efficient vibrational relaxation for low energy electronic excited states (Figure 3B).\(^{(41–43)}\)

For Cu\(^{II}\) in a square pyramidal geometry, the highest Cu d orbital is the \(3z^2\) orbital (see Figure 1 for molecular coordinate definition). The highest occupied orbitals of the superoxide are the doubly degenerate orthogonal \(\pi^*\) orbitals (Scheme 1, \(\pi^*_a\)).

\[ \begin{align*}
\pi^*_a & \quad \pi^*_b \\
\pi^*_c & \quad \pi^*_d \\
\pi^*_e & \quad \pi^*_f \\
\pi^*_g & \quad \pi^*_h \\
\end{align*} \]

\(^{a}\) The arrows and their widths indicate the expected CT transitions and their relative intensities.

Figure 4. Resonance Raman spectra of L3CuO\(_2\) excited at 406.7 nm (~24 590 cm\(^{-1}\)) (A), and L10CuO\(_2\) excited at 482.5 nm (~20 725 cm\(^{-1}\)) (B) in CH\(_2\)Cl\(_2\).

### 3.1.3. Vibrational Spectroscopy

The IR spectrum of the L3CuO\(_2\) complex shows the superoxide O–O vibration at 1112 cm\(^{-1}\), which shifts to 1060 cm\(^{-1}\) upon 18-oxygen substitution (Figure S3).\(^{(18)}\) The previously reported rR O–O vibration of L3CuO\(_2\) at 1111 cm\(^{-1}\) is in fact due to the side-on peroxo dimer L3Cu(O\(_2\))CuL3 component in solution, which has a broad vibrational overtone at 1097 cm\(^{-1}\) with a similar 18-O isotope shift and obscures the superoxide O–O vibration (Figure S1B). (Note that this dimer overtone is not active in IR due to its g symmetry.) Another IR vibrational feature at 550 cm\(^{-1}\) shifts to 532 cm\(^{-1}\) upon 18-oxygen labeling (Figure S3) and is also observed in the resonance Raman spectrum at 554 cm\(^{-1}\) (534 cm\(^{-1}\) in the 18-oxygen labeled sample, Figure 4A). This vibrational mode is assigned as the asymmetric Cu–O stretch.
on the basis of its frequency and isotope shift.\textsuperscript{44} The O–O vibration is observed in the L10CuO\textsubscript{2} resonance Raman spectrum at 1043 cm\textsuperscript{-1} and shifts to 984 cm\textsuperscript{-1} upon 18-oxygen labeling (Figure 4B).\textsuperscript{45} A normal coordinate analysis\textsuperscript{46} on the CuO\textsubscript{2} core using the L3CuO\textsubscript{2} vibrational data and a general valence force field\textsuperscript{47} yields the force constant $k_{O-O} = 5.72$ mdyn/Å, typical of a superoxide O–O bond (Table S1).\textsuperscript{22}

The resonance Raman profile of the L10CuO\textsubscript{2} O–O vibration is included in Figure 3A. It has slight resonance enhancement over the 22 100 cm\textsuperscript{-1} band in the absorption spectrum. This indicates excited-state geometric distortion along the O–O bond and thus some superoxide $\pi^*$ to Cu CT mixing into this $d$–$d$ transition. The $yz$ orbital is the only Cu d orbital with the correct symmetry to mix with the superoxide $\pi^*$ orbitals in the $C_4$ point group (Figure 1) in the excited states, which enables the assignment of the 22 100 cm\textsuperscript{-1} band as the Cu$^{II}$ $yz$ $\rightarrow$ $xy$ transition.

3.2. Calculations. 3.2.1. Electronic Structure Description: Nature of Singlet/Triplet States. Spin-unrestricted density functional calculations were performed on a model complex derived from the L3CuO\textsubscript{2} crystal structure (see Experimental Section), to correlate with the spectroscopic results to gain more insight into the electronic structure of the Cu\textsuperscript{II} superoxo complex. The energy level diagrams and selected MO surface contours of the calculated singlet ground state and lowest triplet state are presented in Figure 5 A and B. Table 1 summarizes the energies and compositions of selected spin-down MOs. Additional MO energies and compositions are given in Tables S2 and S3.\textsuperscript{48}

The calculated ground state is a diamagnetic singlet state (Figure 5A) as experimentally observed (section 3.1.1). All spin-allowed electronic excitations from this ground state involve promoting an electron from an occupied MO to the LUMO of the same spin. We focus our analysis on the spin-down set, which is representative of both spin manifolds (Figure 5A, right, Table 1). The calculated spin-down LUMO of the ground state is the Cu $xy$ orbital, which has a strong antibonding interaction with the superoxide $\pi^*$ orbital (labeled $xy$–$\pi^*_o$, Figure 5A). The superoxide $\pi^*$ level is situated higher in energy than all of the Cu d levels except $xy$ and forms the HOMO, predicting a low-lying $\pi^*_o$ to Cu $xy$ CT singlet excited state. Tetragonal Cu\textsuperscript{II} complexes with innocent ligands do not have ligand field transitions below $\sim$10 000 cm\textsuperscript{-1}.\textsuperscript{37} Thus, the transition observed in the L10CuO\textsubscript{2} absorption spectrum at 4200 cm\textsuperscript{-1} can be associated with this low-lying singlet excited state (Figure 3B).

The intensity of this transition ($\epsilon \approx 200$ M\textsuperscript{-1} cm\textsuperscript{-1}) is consistent with the poor donor/acceptor orbital overlap between $\pi^*_o$ and $xy$–$\pi^*_o$.\textsuperscript{48} The four Cu d levels lie below the superoxide $\pi^*$ level. The Cu $yz$ has the largest mixing with the superoxide $\pi^*$

\begin{table}[ht]
\centering
\begin{tabular}{cccccc}
\hline
level & & singlet ground state & & lowest triplet state & \\
& & $E$ & Cu & O$_2$ & & $E$ & Cu & O$_2$ \\
\hline
$xy$–$\pi^*_o$ & $-0.359$ & 35 & 57 & $xy$–$\pi^*_o$ & $0.509$ & 50 & 40 \\
$\pi^*_o$ & $-1.157$ & 10 & 87 & $\pi^*_o$ & $-1.003$ & 12 & 86 \\
$\pi^*_y$ & $-2.221$ & 82 & 2 & $\pi^*_y$ & $-1.793$ & 85 & 2 \\
$\pi^*_z$ & $-2.956$ & 88 & 5 & $\pi^*_z$ & $-2.415$ & 90 & 4 \\
$\pi^*_x$ & $-3.163$ & 76 & 9 & $\pi^*_x$ & $-2.620$ & 72 & 16 \\
$xy$–$\pi^*_x$ & $-3.439$ & 82 & 4 & $xy$–$\pi^*_x$ & $-2.758$ & 84 & 3 \\
$\pi^*_x$ & $-4.158$ & 33 & 32 & $\pi^*_x$ & $-3.588$ & 38 & 51 \\
\hline

\end{tabular}
\caption{Energies (eV) and Compositions (%) of Spin-Down Cu d and Superoxide $\pi^*$-Based MOs from the Spin-Unrestricted DFT Calculations (ADF) of the Singlet Ground State and the Lowest Triplet State}
\end{table}

(44) The asymmetric Cu–O vibration of the CuO\textsubscript{2} core is not resonance Raman active. Also, the dimeric side-on peroxo component in solution does not have a R feature in this region. See ref 25.

(45) The different O–O vibrational frequency of L10CuO\textsubscript{2} and the L3CuO\textsubscript{2} might be due to the increased ligand strain associated with the bulky adamantyl side chain.

(46) Three internal coordinates (two $r_{O-O}$ and one $r_{O-C}$) were included in the normal coordinate analysis on the CuO\textsubscript{2} three-atom model in C\textsubscript{2v} symmetry. Two different diagonal force constants ($k_{O-O}$, $k_{O-C}$) were included. The introduction of an off-diagonal force constant between the two Cu–O modes is equivalent to increasing $k_{O-O}$ by the same amount. (See: Neese, F.; Solomon, E. I. J. Am. Chem. Soc. 1998, 120, 12829.) This off-diagonal force constant is thus set to zero. An off-diagonal force constant ($k_{O-C}$) between the Cu–O and O–O stretch has a limited effect on the predicted isotope shifts of the two totally symmetric vibrational modes. Varying this interaction force constant between $0.1$ and $0.6$ mdyn/Å does not improve the fit. The force constants reported here were from an analysis using $k_{O-C}=0$ mdyn/Å.


(48) A general electronic structure model for $d^{10}$ metal-superoxido/peroxo complexes was described by Lever and Gray. (Acc. Chem. Res. 1978, 11, 348.) The spectroscopic predictions for the $d^9$ Cu\textsuperscript{II} superoxo complex studied here are different from those of $d^9$/d$^8$ metals due to the presence of only one hole on the Cu atom.

Table 2. Excited Singlet (1'1) and Triplet (1'T) State Energies (cm⁻¹) from Spin-Unrestricted DFT Calculations in ADF on the CuII-Superoxo Complex

<table>
<thead>
<tr>
<th>State</th>
<th>E (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Γ(xyz−π*⁰)</td>
<td>0</td>
</tr>
<tr>
<td>1Γ(xyz)</td>
<td>5515</td>
</tr>
<tr>
<td>1Γ(π*⁰)</td>
<td>2385</td>
</tr>
<tr>
<td>2Γ(z²)</td>
<td>21 025</td>
</tr>
<tr>
<td>3Γ(x²−y²)</td>
<td>25 420</td>
</tr>
<tr>
<td>1Γ(xz)</td>
<td>25 505</td>
</tr>
<tr>
<td>1Γ(ycz)</td>
<td>27 760</td>
</tr>
<tr>
<td>1Γ(π*⁰+xyz)</td>
<td>34 610</td>
</tr>
</tbody>
</table>

* States are labeled by the donor orbitals of the corresponding electronic transitions.

The calculated lowest triplet state is the π*⁰ to Cu CT triplet state at 2385 cm⁻¹ higher in energy than the ground-state singlet (Table 2 and Figure 5B). This triplet state can be associated with the thermally populated triplet state observed in the magnetic susceptibility experiment (Figure 2). The calculated ground-state singlet/triplet splitting is in reasonable agreement with the SQUID measured value (≈1500 cm⁻¹). The spin-down LUMO and LUMO+1 in the triplet MO diagram correspond to the two singly occupied MOs, a spin-restricted representation and indicate that this triplet state has one unpaired electron in the superoxide π*⁰ orbital and the other one in the Cu xy orbital (Figure 5B). This state thus formally correlates to a MO bonding scheme between the CuII atom with a spin in its xy orbital and a superoxide ligand with its spin in its π*⁰ orbital (Scheme 2B). The two spin orbitals are orthogonal to each other, resulting in a triplet state lower in energy than that of the corresponding singlet.

Consequently, the ground singlet state and the lowest triplet state are fundamentally different in nature, and the measured S/T splitting is not 2J as normally used for two localized interacting spins. These two states relate to each other through transfer of one electron between the π*⁰ and xy−π*⁰ orbitals, formally a charge-transfer process. The spin distribution of the singlet ground state is highly delocalized with no spin polarization in contrast to an antiferromagnetic coupling description of its diamagnetism.

3.2.2. Effect of Functional on Spin Polarization. In past studies, it has been found that the extent of spin delocalization can be dependent on the functional chosen. The density functional used above is BP86 in the ADF program. In this section, the density functional is systematically varied by increasing the amount of Hartree–Fock (HF) exchange using a hybrid density functional approach in the Gaussian 98 package. The functionals used include BP86, B3LYP, and B38HFP86, which contain 0, 20, and 38% HF exchange, respectively. The results obtained on the L3CuO₂ crystal structure derived model complex are summarized in Table 3. The calculated MO energy level diagrams and selected MO surface contour plots are given in Figures S5, S6, and S7.

At the pure density functional limit (BP86), the calculated lowest singlet and triplet states of the CuII-superoxo complex are similar to the results obtained from ADF calculations (Figures S5 and S5). The triplet state is higher in energy than the singlet with a S/T splitting of 643 cm⁻¹, qualitatively...
consistent with experiment (Figure 2, Table 3). Upon including the triplet state drops below the singlet state (S/T = 1, paramagnetic). Concomitant with this, the singlet state becomes more spin polarized. Opposite spin densities localize on the Cu and the superoxide (Cu: −0.54 spin, superoxide: 0.60 spin, in the B38HFP86 calculation, Table 3), leading to a singlet state where the interaction is reasonably described as an antiferromagnetic exchange coupled system. Additionally, the Cu d manifold shifts to lower energy and drops below the superoxide π°\textsubscript{e} level as the HF exchange is increased in the density functional calculations (Figures S6 and S7).

Because the lowest singlet and triplet states involve different bonding interactions between the Cu\textsuperscript{II} and the superoxide (Scheme 2), the molecular geometries could be different for these two states. (The L\textsubscript{3}Cu\textsubscript{O}_{2}\textsuperscript{−} crystal structure is associated with the singlet state geometry, which is used for the above calculations.) To account for the possible effect of different geometries on the relative energies of the singlet and the triplet states, geometry optimizations were also performed for both states with different functionals. Table 4 summarizes the optimized geometries, calculated S/T splitting, and the singlet spin distributions. The calculated O–O bond of the singlet is longer than that in the L\textsubscript{3}Cu\textsubscript{O}_{2}\textsuperscript{−} crystal structure with all three functionals. Within each functional, the O–O bond at the triplet state is slightly shorter than that at the singlet state, while the Cu–O bond is longer. This is consistent with their different bonding interactions because the triplet state derives formally from a superoxide π°\textsubscript{e} → xy–π°\textsubscript{e} CT process from the singlet state (Scheme 2). This CT process moves electron density from a mainly superoxide O–O antibonding orbital (π°\textsubscript{e}) to a mainly Cu–O antibonding orbital (xy–π°\textsubscript{e}) and thus leads to the shortened O–O and elongated Cu–O bond in the triplet state. The calculated S/T splitting with geometry optimizations shows the same trend and similar magnitudes as those obtained in the above calculations based on the crystal structure. At the pure density functional limit (BP86), the singlet is the ground state, and the triplet is 742 cm\textsuperscript{−1} higher in energy (Table 4), qualitatively consistent with experiment (Figure 2, Table 3). With increasing HF exchange included in the functional, the triplet state drops below the singlet state (S/T < 0) to become the ground state. The singlet state concomitantly becomes more spin polarized with opposite spin densities localized on the Cu and the superoxide (Cu: −0.59 spin, superoxide: 0.68 spin, in the B38HFP86 calculations, Table 4), corresponding more to an antiferromagnetic exchange coupled system.

The magnetic susceptibility data in Figure 2 show that the ground state of the Cu\textsuperscript{II}-superoxide complex is a diamagnetic singlet state with the lowest triplet state ~1500 cm\textsuperscript{−1} higher in energy (section 3.1.1). The electronic absorption spectrum (Figure 3) indicates that the Cu d manifold is above the superoxide π°\textsubscript{e} level in energy (section 3.1.2). Correlating these experimental results with the results obtained with different density functionals indicates that the pure density functional BP86 gives the most reasonable description of the electronic structure of the Cu\textsuperscript{II}-superoxide complex. The ground-state singlet in the pure DFT calculation is highly delocalized with no spin localization (Tables 3 and 4), consistent with the results obtained in section 3.2.1 and indicating that an antiferromagnetic coupled description is not appropriate for the ground-state diamagnetism of the Cu\textsuperscript{II}-superoxide complex.

4. Discussion

A combination of spectroscopic characterization and DFT calculations has provided a detailed electronic structure description of the monomeric side-on Cu\textsuperscript{II}-superoxide complex. The Cu\textsuperscript{II}-superoxide complex has a diamagnetic singlet ground state and a low-lying triplet state at ~1500 cm\textsuperscript{−1} higher in energy. The singlet ground state involves a strong interaction between the Cu xy and the superoxide π°\textsubscript{e} orbital (Scheme 3, bottom). The lowest triplet state involves the interaction between the orthogonal Cu xy and the superoxide π°\textsubscript{e} orbital and has a fundamentally different orbital configuration from the ground-state singlet (Scheme 3, top). This triplet state is related to the ground-state singlet through a superoxide π°\textsubscript{e} to Cu xy CT process (Scheme 2), and the corresponding π°\textsubscript{e} excited singlet state is observed at 4200 cm\textsuperscript{−1} in the electronic absorption spectrum (Figure 3B).

The relative energy of the π°\textsubscript{e} triplet state to the π°\textsubscript{e} singlet ground state is related to the splitting (ΔE) of the two singly occupied molecular orbitals in a spin-restricted representation (xy–π°\textsubscript{e} and π°\textsubscript{e}, Scheme 2B), which correspond to the spin-down LUMO+1/LUMO (xy–π°\textsubscript{e}/π°\textsubscript{e}) in the spin-unrestricted description (see Figure 5B). Decreasing the xy–π°\textsubscript{e}/π°\textsubscript{e} splitting, ΔE, will stabilize the triplet state which eventually becomes the ground state, whereas a large ΔE will destabilize the triplet and eventually overcome the electron repulsion for spin pairing leading to the π°\textsubscript{e} singlet ground state (Scheme 2A). This trend is reflected in singlet/triplet state ordering calculated using

**Table 3.** Density Functional Dependence of the Calculations on the Cu\textsuperscript{II}-Superoxide Complex

<table>
<thead>
<tr>
<th></th>
<th>BP86</th>
<th>B3LYP</th>
<th>B38HFP86</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/T splitting (cm\textsuperscript{−1})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu: −0.01; O\textsubscript{2}; Cu: −0.54; O\textsubscript{2}; O\textsubscript{2}; O\textsubscript{2}; O\textsubscript{2}; 0.01</td>
<td>643</td>
<td>−1844</td>
<td>−4882</td>
</tr>
<tr>
<td>ΔE(xy−π\textsubscript{e}/π\textsubscript{e}) (eV)</td>
<td>1.10</td>
<td>0.94</td>
<td>0.81</td>
</tr>
<tr>
<td>π°\textsubscript{e} composition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu\textsuperscript{II}, Cu\textsuperscript{II}, Cu\textsuperscript{II}, Cu\textsuperscript{II}, Cu\textsuperscript{II}, Cu\textsuperscript{II}</td>
<td>43% O\textsubscript{2}, 47% O\textsubscript{2}, 40% O\textsubscript{2}, 33% O\textsubscript{2}, 1% O\textsubscript{2}, 6% Cu\textsuperscript{II}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>π°\textsubscript{e} orbital energy splitting (LUMO) orbital energy splitting of the lowest triplet state</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>94% O\textsubscript{2}, 98% O\textsubscript{2}, 99% O\textsubscript{2}, 64% Cu\textsuperscript{II}, 95% Cu\textsuperscript{II}, 99% Cu\textsuperscript{II}, 99% Cu\textsuperscript{II}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) S/T = E(triplet) − E(singlet). (b) Spin densities on the Cu atom and the superoxide of the lowest singlet state. (c) Spin-down xy–π\textsubscript{e}/π\textsubscript{e} (LUMO+1/LUMO) orbital energy splitting of the lowest triplet state. (d) Spin-down xy–π\textsubscript{e} and π°\textsubscript{e} orbital compositions of the lowest triplet state.
different functionals. The B3LYP86 calculations give a small \( xy-\pi^*_o/\pi^*_o \) splitting (\( \Delta E = 0.81 \) eV, Table 3), leading to the triplet state lower than the singlet, contrary to the experimental result. Alternatively, the BP86 calculations give a larger splitting (\( \Delta E = 1.10 \) eV, Table 3), and a ground-state singlet/triplet energy ordering consistent with experiment is obtained (calculated \( S/T = 643 \) cm\(^{-1} \), Table 3, experimental \( S/T \approx 1500 \) cm\(^{-1} \)).

The smaller \( xy-\pi^*_o/\pi^*_o \) splitting \( \Delta E \) in the B38HF86 calculation results from the increased HF exchange in the functional, which shifts the Cu d manifold up in energy relative to the superoxide \( \pi^* \) valence orbitals and thus increases their energy separation (\( \Delta \text{ML} \), Scheme 2B).\(^{28}\) From perturbation theory,\(^{52}\) the increased \( \Delta \text{ML} \) would lead to a weakened interaction between the Cu \( xy \) and the superoxide \( \pi^*_o \) orbital and thus reduce the magnitude of the antibonding orbital destabilization energy (\( X = 1/\Delta \text{ML} \), Scheme 2B). This is reflected in the covalency of the \( xy-\pi^*_o \) orbital, where the B38HF86 calculation has more Cu character and is thus less covalent due to the increased \( \Delta \text{ML} \) (59\% Cu + 33\% O\(^2^-\), Table 3). This results in a smaller \( xy-\pi^*_o/\pi^*_o \) splitting \( \Delta E \) and the triplet as the ground state in the B38HF86 calculation. Comparatively, the BP86 calculation gives a more covalent Cu \( xy \) and superoxide \( \pi^*_o \) interaction (43\% Cu + 47\% O\(^2^-\), Table 3), and thus \( \Delta E \) is large enough to overcome the electron repulsion for spin pairing, leading to the singlet ground state (Scheme 2A, Table 3).

The strong covalent interaction between the Cu \( xy \) and the superoxide \( \pi^*_o \) orbital also leads to a large separation of the corresponding bonding/antibonding orbitals (\( xy-\pi^*_o/\pi^*_o \), Scheme 2A). This gives rise to the high energy of the \( \pi^*_o \) to Cu \( xy \) CT state. It also leads to a very high energy \( xy/\pi^*_o \) triplet state, which correlates to an electron configuration having one spin-up electron in the \( xy-\pi^*_o \) and the second spin-up electron in the \( \pi^*_o+xy \) orbital. This is formally a superoxide \( \pi^*_o \) to Cu \( xy \) CT triplet state and is calculated to be at 26 430 cm\(^{-1} \) (\( 3\tilde{\Gamma}(\pi^*_o+xy) \), Table 2).

The energy separation of the \( xy-\pi^*_o \) and \( \pi^*_o+xy \) molecular orbitals also affects the extent of spin polarization of the ground-state singlet.\(^{53,54}\) These two MOs are linear combinations of interacting Cu \( xy \) and superoxide \( \pi^*_o \) orbitals, each of which carries a single spin before interaction (Scheme 2A). From these two MOs, the many-electron configurations arise (Scheme 4, \( \phi_1 \approx \pi^*_o+xy \), \( \phi_2 \approx xy-\pi^*_o \)).\(^{53,54}\)

The lowest singlet state wave function of the system \( \psi_S \) will be a linear combination of \( S_1 \), \( S_2 \), and \( S_3 \):\(^{55}\)

\[
\psi_S = \lambda_1 \psi_{S_1} + \lambda_2 \psi_{S_2} + \lambda_3 \psi_{S_3} \tag{1}
\]

while the triplet state is well represented by \( \psi_T \). (Note that the triplet state here is fundamentally different from the lowest triplet state discussed above, which involves the superoxide \( \pi^*_o \) orbital.) When the energy separation of \( \phi_1 \) and \( \phi_2 \) is small (weak interaction limit), \( |\lambda_1| \approx |\lambda_2| \approx |\lambda_3| \), and the strong mixing between \( S_1 \) and \( S_2 \) would lead to the ground-state wave function \( \psi_S \) highly polarized with opposite spin densities localized on the Cu and the superoxide, corresponding to an antiferromagnetically coupled singlet state. If the energy splitting of \( \phi_1/\phi_2 \) is large (strong interaction limit), \( |\lambda_1| \gg |\lambda_2|, |\lambda_3| \), and the wave function \( \psi_S \) is delocalized with no spin polarization. This is the case for the mononuclear side-on superoxo-Cu\(^{II} \) complex. A highly covalent interaction between the Cu \( xy \) and superoxide \( \pi^*_o \) orbitals leads to a large energy separation of \( \phi_1 \) and \( \phi_2 \), and the resulting ground-state singlet is highly delocalized with no spin polarization (Figure 6A). In contrast, the B38HF86 calculation gives a less covalent interaction between the Cu \( xy \) and superoxide \( \pi^*_o \) orbital and thus a smaller energy separation of \( \phi_1 \) and \( \phi_2 \). This leads to the calculated singlet state being highly spin polarized (Figure 6B) and an opposite singlet/triplet energy ordering as compared to experiment.


(54) Here, all MOs are from high-spin (triplet) calculations.

(55) Note here that \( S_1, S_3 \) all have the same symmetry.

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**Table 4.** Optimized Geometries for Both Singlet and Triplet States with Different Density Functionals on the Cu\(^{II} \)-Superoxo Complex

<table>
<thead>
<tr>
<th></th>
<th>( r(O-O) (\text{Å}) )</th>
<th>( r(\text{Cu}-O) (\text{Å}) )</th>
<th>S/T splitting (cm(^{-1} ))</th>
<th>singlet spin distribution(^b)</th>
<th>( \text{BP86} )</th>
<th>( \text{B3LYP} )</th>
<th>( \text{B38HF86} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>singlet</td>
<td>1.362</td>
<td>1.326</td>
<td>742</td>
<td>Cu: 0.01; O(_2): 0.01</td>
<td>1.356</td>
<td>1.311</td>
<td>1.325</td>
</tr>
<tr>
<td>triplet</td>
<td>1.857</td>
<td>1.959</td>
<td></td>
<td>Cu: 0.00; O(_2): 0.00</td>
<td>1.813</td>
<td>1.952</td>
<td>1.854</td>
</tr>
</tbody>
</table>

\(^a\) S/T = \( E(\text{triplet}) - E(\text{singlet}) \). \(^b\) Spin densities on the Cu atom and the superoxide of the lowest singlet state.

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**Figure 6.** Two-dimensional CuO\(_2\) plane \( xy-\pi^*_o \) MO contours from Gaussian 98 calculations. (A) Delocalized spin-up (top) and spin-down (bottom) \( xy-\pi^*_o \) orbitals of the Cu\(^{II} \)-superoxo complex from the unrestricted BP86 singlet state calculation. Both orbitals have similar Cu/O\(_2\) character (27\% Cu + 66\% O\(_2\)). (B) Polarized spin-up (top, 59\% Cu + 31\% O\(_2\)) and spin-down (bottom, 8\% Cu + 88\% O\(_2\)) \( xy-\pi^*_o \) orbitals from the unrestricted B38HF86 singlet state calculation.

---

**Scheme 4**

\[ \phi_1, \phi_2, \phi_3, \phi_4 \]

\[ S_1, S_2, S_3, S_4 \]

\[ T, \phi, \beta, \alpha \]

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In summary, the diamagnetic singlet ground state of the mononuclear side-on superoxo-CuII complex results from the highly covalent interaction between the Cu $xy$ and the superoxide $\pi^*$ orbitals. The large covalency leads to a singlet ground state with no spin polarization; thus, it is inappropriate to describe this as an antiferromagnetic coupled system. The lowest triplet state is fundamentally different in electronic origin from the ground-state singlet and involves the Cu $xy$ and the superoxide $\pi^*$ orbital. This $\pi^*$ triplet is related to a very low energy singlet $\pi^*$ CT transition at 4200 cm$^{-1}$ above the ground-state singlet. Thus, the singlet/triplet splitting observed experimentally does not reflect antiferromagnetic exchange coupling, but rather a low energy charge-transfer process.

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Supporting Information Available: L3CuO2 solution absorption and resonance Raman (Figure S1), L10CuO2 null absorption (Figure S2), L3CuO2 IR spectra (Figure S3), L1CuII(OH)2-CuII L1 null absorption (Figure S4), additional MO energy level diagrams and contour surface plots (Figures S5–S7), normal coordinate analysis results (Table S1), additional MO energies and compositions (Tables S2 and S3), and molecular coordinates (Table S4) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.