Electronic Structure of a Cu$^{II}$–Alkoxide Complex Modeling Intermediates in Copper-Catalyzed Alcohol Oxidations

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Supporting Information

ABSTRACT: In the copper-catalyzed oxidation of alcohols to aldehydes, a Cu$^{II}$-alkoxide (Cu$^{II}$–OR) intermediate is believed to modulate the αC–H bond strength of the deprotonated substrate to facilitate the oxidation. As a structural model for these intermediates, we characterized the electronic structure of the stable compound Tp$^{Bu}$Cu$^{II}$(OCH$_2$CF$_3$)$_3$ (Tp$^{Bu}$ = hydrotris(3-tert-butyl-pyrazolyl)borate) and investigated the influence of the trifluoroethoxide ligand on the electronic structure of the complex. The compound exhibits an electron paramagnetic resonance (EPR) spectrum with an unusually large $g_{\perp}$ value of 2.44 and a small copper hyperfine coupling $A_{\perp}$ of 40 × 10$^{-4}$ cm$^{-1}$ (120 MHz). Single-crystal electron nuclear double resonance (ENDOR) spectra show that the unpaired spin population is highly localized on the copper ion (~68%), with no more than 15% on the ethoxide oxygen. Electronic absorption and magnetic circular dichroism (MCD) spectra show weak ligand-field transitions between 5000 and 12 000 cm$^{-1}$ and an intense ethoxide-to-copper charge transfer (LMCT) transition at 24 000 cm$^{-1}$, resulting in the red color of this complex. Resonance Raman (rR) spectroscopy reveals a Cu–O stretch mode at 592 cm$^{-1}$. Quantum chemical calculations support the interpretation and assignment of the experimental data. Compared to known Cu$^{II}$-thiolate and Cu$^{II}$-alkylperoxo complexes from the literature, we found an increased $\sigma$ interaction in the Cu$^{II}$–OR bond that results in the spectroscopic features. These insights lay the basis for further elucidating the mechanism of copper-catalyzed alcohol oxidations.

INTRODUCTION

Copper($II$)/radical systems are important catalysts for the oxidation of alcohols to aldehydes in both biology and synthesis. In nature, the fungal copper enzyme galactose oxidase (GAO) converts primary alcohols to aldehydes.1,2 In organic synthesis, Cu/nitroxyl systems catalyze the same oxidation.3–5 The currently accepted mechanisms of both biological and synthetic alcohol oxidation propose Cu$^{II}$-alkoxide complexes as relevant intermediates.6,7 Deprotonation of the alcohol when it binds to copper is expected to significantly weaken the substrate αC–H bond strength in preparation for oxidation.8

During substrate oxidation in GAO, an alcohol binds to the Cu$^{II}$ site and is deprotonated by an axially bound tyrosinate ligand, producing the proposed Cu$^{II}$-alkoxide intermediate. Ultimately H atom transfer (HAT) to a coordinated 3'-(S-cysteinyl)tyrosinate radical9,10 and electron transfer produce the aldehyde product and Cu$^{I}$. However, the extent of kinetic coupling between the steps is still under investigation.6,11 For the synthetic Cu/nitroxyl systems, several mechanisms of alcohol oxidation have been discussed in the literature. They all include a Cu$^{II}$-alkoxide as the first intermediate and differ in the binding mode of the exogenous nitroxyl moiety (which abstracts the αC–H hydrogen of the substrate producing the aldehyde product).12–16

Understanding the geometric and electronic structure of these intermediates, including the extent to which the αC–H bond in the alcohol substrate is activated by copper, is of crucial importance to gain further insight into the mechanisms of both GAO and the synthetic Cu/nitroxyl systems. However, a detailed electronic structure characterization has not been performed on these intermediates and very few small molecule Cu$^{II}$-alkoxide complexes are known in the literature to serve as models.17–20

As a step toward understanding the structure of the intermediates in Cu-mediated alcohol oxidation, we examined a Cu$^{II}$-alkoxide complex, Tp$^{Bu}$Cu$^{II}$(OCH$_2$CF$_3$)$_3$ (abbreviated Cu$^{II}$–O(TFE) throughout). This complex does efficient H atom abstraction when treated with H atom donors such as TEMPO–H, yielding the corresponding radical, trifluoroethanol, and Cu$^{II}$. While this complex is not a direct functional model (i.e., alkoxide oxidation does not occur upon treatment with external oxyl radical H atom acceptors),21 it serves as a general structural model for the proposed intermediates in Cu/
radical alcohol oxidation systems. The complex, shown in Figure 1, features a tridentate Tp\(^{tBu}\) (Tp\(^{tBu}\) = hydro-tris(3-tert-butyl-pyrazolyl)borate) ligand scaffold and a 2,2,2-trifluoroethoxide ligand. Structurally, the bulky Tp\(^{tBu}\) ligand mimics the catalyst/enzyme supporting ligands, and the alkoxide functions as a substrate model. The complex has an approximately trigonal monopyramidal coordination geometry with a long Cu−N\(_{axial}\) bond (similar to type 1 copper sites). Here, we characterized the electronic structure of Cu\(^{II}\)−O(TFE). We used powder and single-crystal electron paramagnetic resonance (EPR) spectroscopy to probe the paramagnetic S = 1/2 ground state. This revealed the identity of the singly occupied molecular orbital (SOMO), the d\(^{x^2−y^2}\), and its orientation within Cu\(^{II}\)−O(TFE). It also revealed a large shift in g\(_{zz}\) (one of the largest recorded for copper in a biologically relevant ligand scaffold) and a small copper hyperfine Cu\(^{II}\)A\(_{zz}\), (similar in magnitude to type 1 blue copper sites). Using electron nuclear double resonance (ENDOR) spectroscopy, we measured the hyperfine couplings to determine the strength of the interaction between the unpaired electron and nearby magnetic nuclei (\(^1\)H, \(^{19}\)F, \(^{14}\)N). With these values, we mapped the extent of delocalization of the unpaired electron onto the Tp\(^{tBu}\) and trifluoroethoxide ligands and found much of the spin population localized on copper. Using UV−vis−NIR, magnetic circular dichroism (MCD), and resonance Raman (rR) spectroscopies, we assigned the electronic transitions and characterized the nature of the Cu−O bond. We show Cu\(^{II}\)−O(TFE) has a near-UV ethoxide-to-copper charge transfer transition, giving it a red color, reminiscent of biological red copper sites (nitrosocyanin and BSco). We compare Cu\(^{II}\)−O(TFE) to analogous thiolate (Cu\(^{II}\)−SR) and peroxo (Cu\(^{II}\)−OOR) ligated copper compounds to understand the influence of the ethoxide ligand on electronic structure. In addition, we summarize how the identifying spectroscopic features (large g\(_{zz}\), small Cu\(^{II}\)A\(_{zz}\), near-UV transition) are related to biological copper sites.

Our data allow the following conclusions to be made. First, the spin population on the ethoxide ligand is small, leaving much of the spin localized on copper. The absence of substantial spin population on the ethoxide ligand suggests a relatively ionic Cu−O bond compared to related Cu\(^{II}\)−O(TFE)−d\(_2\).
complexes with similar distorted tetrahedral ligand environments. Despite the relatively ionic Cu–O bond, the αC–H bond of the trifluoroethoxide is not activated enough to promote ligand oxidation. Second, the Cu–O bond has contributions from both Cu $d_{xz}/O$(TFE) $p_{\sigma}$ and Cu $d_{yz}/O$(TFE) $p_z$ interactions. The σ bonding interaction between the O(TFE)-based $p_{\sigma}$ and the copper-based $d_{xy}$ orbitals reduces the energy gap between the dominantly $d_{xy}$ antibonding orbital and the singly occupied $d_{yz}$ orbital. This results in the small difference in energy, $E_{d_{xy}} - E_{d_{yz}}$ observed by MCD spectroscopy, that drives the large shift in $g_{xx}$. Overall, these insights contribute to the understanding of the role of alkoxide intermediates in CuII-catalyzed alcohol oxidations.

**RESULTS**

**Field-Swept EPR.** A combination of 9.2 GHz (X-band) and 34 GHz (Q-band) EPR spectroscopies reveal the magnetic parameters of the CuII-alkoxide. The continuous-wave (CW) 9.2 GHz EPR spectrum of CuII–O(TFE) in a frozen solution of toluene at 120 K is shown in Figure 2A. This spectrum resolved the unusually large $g_{xx} = 2.44(1)$ and small Cu hyperfine coupling $A_{hF} = 120(10)$ MHz ($40(3) \times 10^{-4}$ cm$^{-1}$). 34 GHz EPR, shown in Figure 2B, of CuII–O(TFE) in DCM:toluene at 10 K further resolved the principal values of the $g$ tensor. The data and simulations indicate the tilting $g_{zz} \approx 2.0023$ indicates that the molecule is in a nearly normal to the long Cu–O bond of the trifluoroethoxide ligand and the singly occupied $d_{yz}$ orbital lies in a plane normal to the $g$ axis. As a result, we determined the lobes of the singly occupied $d_{yz}$ orbital lie in a plane normal to the $z$ axis and nearly normal to the long Cu–N$_{aryl}$ bond. Figure S6A shows the orientations of the static field in the molecule for this set of spectra.

**ENDOR.** $^1$H ENDOR. To quantify the distribution of unpaired spin population in the molecule, we measured the hyperfine coupling interaction between the unpaired electron and surrounding magnetic nuclei using ENDOR spectroscopy. Frozen-solution ENDOR spectra of CuII–O(TFE) revealed broad $^1$H peaks split by $\approx 25$ MHz and centered around the $^1$H Larmor frequency (peaks at $\pm 12$ MHz in Figure S4). In ENDOR spectra of CuII–O(TFE), $d_{xy}$ these features shifted to lower frequency (centered at the $^1$H Larmor frequency). This indicates these features originate from the αC–H protons on the trifluoroethoxide ligand and these protons have isotropic hyperfine couplings of about 25 MHz.

To determine the full hyperfine tensors of the two protons, including principal values and tensor orientations, we measured $^1$H ENDOR on a doped single crystal (1% CuII–O(TFE), 99% ZnII–O(TFE)). The corresponding spectra in Figure 4 show two pairs of orientation-dependent hyperfine lines due to the two ethoxide protons which we named H$_r$ and H$_g$ (referring to the prochirality of the hydrogens pictured in Figure 1). The total hyperfine coupling $A_{tot}$ for each proton is modeled as the sum of an isotropic term and an anisotropic dipolar term, $A_{tot} = A_{iso} + A_{dip}$. The dipolar term of the hyperfine coupling produces the curved path of the peaks in the series of spectra collected as the orientation of the single crystal is rotated in the magnetic field.

![Figure 3. Orientation of the g tensor in CuII–O(TFE) determined from single-crystal EPR. An axial g tensor ellipsoid is centered on copper and the $x_g$, $y_g$, and $z_g$ axes of the tensor are shown as thick red, green, and blue lines, respectively. (A) The $z_g$ axis lies 10° off the Cu–N$_{aryl}$ bond in crystal 1 (10° in crystal 2, see SI). (B) The $y_g$ axis lies 22° off the Cu–O bond in crystal 1 (37° in crystal 2, see SI).](image)

Importantly, the dipolar term depends on the distance between the $^1$H nucleus and the unpaired spin, which is delocalized in the molecule. We modeled the dipolar hyperfine coupling with a distributed point-dipole approximation assuming the spin population of the $d_{yz}$ ground state was distributed across the copper, the oxygen of the trifluoroethoxide ligand, and the two basal nitrogen atoms of the Tp$^{6u}$ ligand (roughly the $xy$ plane). For each proton, H$_r$ and H$_g$, the total dipolar hyperfine tensor is the sum of four dipolar subtensors

$$A_{dp,i} = \sum \sigma_i A_{dp,i}$$

where $\sigma_i$ represents the spin population on atom $i$ for $i = Cu, O, N1, N2$. Each subtensor was calculated using the point-dipole approximation

$$A_{dp,i} = \frac{\mu_B}{4\pi} \mu_H N_S g_S S \sum_{i=1}^3 \left( r_{Hi}^T \left( \frac{3r_{Hi}r_{Hi}^T}{r_{Hi}^2} - 1 \right) \right)$$

Here $\mu_B$ is the Bohr magneton, $\mu_H$ is the nuclear magneton, $g_N$ is the nuclear g value, $I$ is the $3 \times 3$ identity matrix, $\mu_B$ is the vacuum permeability, and $g$ is the full $3 \times 3$ g tensor obtained from fitting the single crystal pulse-field swept spectra. The distance vectors $r_{Hi}$ were taken directly from the coordinates of the X-ray crystal structure. In our simulations, the isotropic
The proximity of the oxygen atom to the $^1$H nuclei meant the dipolar contribution to the simulation was affected most significantly by the spin population on oxygen, $\sigma_O$. Even after significantly decreasing the spin density on copper ($\sigma_{Cu} = 0.4$), values for $\sigma_O$ any larger than 0.15 produced simulations with too large a dipolar component. However, because the results of $^{14}$N ENDOR spectroscopy (in agreement with DFT calculations, see below) place upper bounds of 0.10 on both $\sigma_{N1}$ and $\sigma_{N2}$, it is reasonable to conclude $\sigma_{Cu}$ is no less than 0.6. With $\sigma_{Cu} = 0.6$, values of $\sigma_O$ any greater than 0.13 produced simulations with too large a dipolar coupling, allowing us to use this as an upper bound for spin population on oxygen in the single crystal.

Specifically, the values $\sigma_{N1} = 0.09$ (or 9%) and $\sigma_{N2} = 0.05$ (or 5%) were chosen based on $^{14}$N ENDOR data and are supported by DFT calculations as discussed below. Isotropic couplings, $A_{iso,H3} \approx 25.8$ MHz and $A_{iso,H5} = 8$ MHz were used in the simulations and translate to spin populations on the protons of 0.018 (1.8%) and 0.006 (0.6%) respectively. The remainder of the spin population ($0.836, 83.6\%$) was split significantly by the spin population on oxygen, $\sigma_O$, $\sigma_{Cu}$, $\sigma_{N1}$, and $\sigma_{N2}$; the principal values of the dipolar coupling were computed as ($-3.3, -2.6, 6.3$) MHz for $H_3$ and ($-2.5, -3.1, 5.5$) MHz for $H_5$ using eq 1 and 2 (tensor orientations shown in Figure S6B). The resulting principal values of the hyperfine coupling are ($4.7, 5.4, 14$) MHz for $H_3$ and ($23, 23, 31$) MHz for $H_5$ (summarized in Table S1C). These values for $A_{iso,H3}$, $A_{iso,H5}$, $\sigma_{Cu}$, $\sigma_{N1}$, and $\sigma_{N2}$ also produced satisfactory simulations of $^1$H ENDOR spectra for a second single crystal (Figure S3, Table S1C). These data suggest a relatively ionic Cu–O bond with little spin delocalization onto the trifluoroethoxide ligand.

The hyperfine couplings for $H_R$ and $H_5$ are dependent upon the site in the crystal unit cell used for the calculations. The two sites are related by a mirror plane which exchanges the dihedral hyperfine coupling values ($A_{iso,H5}, A_{iso,H3}$) and the spin populations ($\sigma_{Cu}, \sigma_{N1}, \sigma_{N2}$) were adjustable parameters.

Figure 4. Single-crystal $^1$H ENDOR resolves the hyperfine tensors of the trifluoroethoxide ligand protons $H_5$ and $H_3$. (Top) The isotropic hyperfine couplings are marked by a black line and the spread of the dipolar hyperfine couplings ($A_{dp} \approx 9$ MHz) is marked by a gray box. Shown in blue are echo-detected Davies ENDOR spectra [$\pi(80 \text{ ns}) - T - \pi/2(40 \text{ ns}) - \tau(230 \text{ ns}) - \pi(80 \text{ ns}) - \tau - \text{echo}$] of 1% Cu$^{II}$–O(TFE) in a Zn$^{II}$–O(TFE) single-crystal. Spectra were acquired at 34.151 GHz (0–75°) and 34.143 GHz (90–180°) (10 K, 3 ms repetition time). A 13 μs RF pulse was applied to excite nuclear transitions and was stepped in 0.1 MHz increments. Spectra were acquired at the $g$ values corresponding to the transitions marked with a dotted line in Figure 2C. Simulations are shown in green (parameters in Table S1C).

Figure 5. $^{19}$F and $^{14}$N ENDOR spectra of a frozen solution of Cu$^{II}$–O(TFE)–$d_2$ (A) and Cu$^{II}$–O(TFE) (B) in a DCM:toluene glass (10 K, 3 ms repetition time). (A) Shown in blue are echo-detected Davies ENDOR spectra [$\pi(100 \text{ ns}) - T - \pi/2(50 \text{ ns}) - \tau(240 \text{ ns}) - \pi(100 \text{ ns}) - \tau - \text{echo}$] acquired at 34.068 GHz at the fields corresponding to $g$ values listed in the figure. A 15 μs RF pulse was applied in 0.05 MHz steps. The $^{19}$F dipolar hyperfine coupling for simulations (green, parameters in Table S1D) were calculated with the distributed point dipole approximation assuming spin populations of $\sigma_{f} = 0.15$ and $\sigma_{m} = 0.68$. (B) Shown in blue are echo-detected Davies ENDOR spectra [$\pi(80 \text{ ns}) - T - \pi/2(40 \text{ ns}) - \tau(240 \text{ ns}) - \pi(80 \text{ ns}) - \tau - \text{echo}$] acquired at 34.118 GHz at the fields corresponding to $g$ values listed in the figure. A 14.5 μs RF pulse was applied. The $^{14}$N hyperfine couplings for simulations (green, parameters in Table S1D) are marked at the $A/2$ value (nitrogen in the strong coupling regime) for spectra acquired at $g = 2.45$ (bottom) and $g = 2.05$ (top). These coupling correspond to spin populations on the basal Tp$^{6}$ nitrogen atoms of $\sigma_{N1} = 0.09$ and $\sigma_{N2} = 0.05$. DOI: 10.1021/jacs.5b13088

angles (i.e., Cu–O–C–H$_2$ = −81.06° and Cu–O–C–H$_2$ = 37.43° become Cu–O–C–H$_2$ = −37.43° and Cu–O–C–H$_2$ = 81.06°). This exchanges the values of the hyperfine coupling and spin populations of the two protons.

$^{19}$F ENDOR. Higher resolution ENDOR spectra of a frozen solution of Cu$_{12}$–O(TFE) near the $^1$H Larmor frequency show a peak pattern that is slightly asymmetric (Figure S5). This is due to fluorine peaks centered at the $^3$P Larmor frequency, which is 2.9 MHz lower than the $^1$H Larmor frequency at 1160 mT. To separate the fluorine peaks from the proton peaks, the higher frequency half of the $^1$H ENDOR spectrum, which contains purely proton features, was subtracted from the lower frequency half of the ENDOR spectrum. This yielded the difference spectrum in Figure 5A with $^1$F peaks only. Due to the three- to four-bond distance between the fluorine nuclei and the majority of the spin density, the isotropic hyperfine coupling was assumed to be negligible. Satisfactory simulations of these data were performed assuming a purely dipolar hyperfine coupling. The dipolar coupling principal values were computed using the distributed point-dipole approximation as described above using distance vectors obtained from crystal coordinates. To achieve the simulations shown in Figure 5A, the spin population of oxygen, $\sigma_O$, was increased to 0.15(3) and the spin population of copper, $\sigma_{Cu}$, decreased to 0.68(3) while the nitrogen spin populations were kept as 0.09 and 0.05.

Principal $^1$H hyperfine values of (−1.1, −1.4, 2.4) MHz, (−0.65, −0.75, 1.4) MHz, and (−1.1, −1.3, 2.2) MHz were calculated (Table S1D). Hyperfine tensor frames were defined using the crystal structure coordinates assuming the unique axis ($A_{zz}$) points toward the copper nucleus (see Experimental Section for details) and are visualized in Figure S6B. These simulations reproduce the orientation dependence and width of the spectra well, which supports the small $\sigma_O$ and allows us to place an upper bound of 15 ± 3% spin population on oxygen when Cu$_{12}$–O(TFE) is in a frozen solution consistent with the small $\sigma_O$ observed for the single crystal.

$^{14}$N ENDOR. Orientation-dependent 34 GHz $^{14}$N ENDOR supports the spin delocalization onto the Tp$_{Bu}$ ligand (Figure S3). At the low-field position (993 mT, $g_{zz} = 2.45$) where strong orientation selection is expected, the ENDOR spectrum shows only two features at 11.5 and 17.5 MHz. These features are split by twice the Larmor frequency of $^{14}$N (3.05 MHz) and spin population on other atoms (Cu, O, other N) were determined to be negligible (<1 MHz) using the point-dipole approximation. In addition, we observed weak modulations in an ESEEM experiment (see SI section 1.g, Figure S7) that are likely due to the axial nitrogen. Since hyperfine coupling and spin population on the axial nitrogen are expected to be weak based on DFT calculations ($A_{iso} < 1$ MHz), this was not considered in the distributed point dipole approximation.

Electronic Spectroscopy. With a combination of room temperature electronic absorption (RT ABS), low temperature electronic absorption (LT ABS), and MCD spectroscopy, we resolved the near-UV and near-IR electronic transitions of Cu$_{12}$–O(TFE) (Figure 6). The RT ABS spectrum (Figure 6A) shows an intense near-UV transition at 24 000 cm$^{-1}$ ($\epsilon \approx 3000$ M$^{-1}$ cm$^{-1}$) which is not present in the precursor Tp$_{Bu}$Cu$_{12}$OTf. Additional weak near-IR features ($\epsilon < 300$ M$^{-1}$ cm$^{-1}$) are seen below 13 000 cm$^{-1}$. In the MCD spectrum (Figure 6C), two transitions underlying the near-UV transition become distinguishable. The near-IR features in the MCD spectrum are resolved into four distinct features which grow in intensity relative to the near-UV features.

Based on the resolution of the MCD spectrum we chose to model our electronic transitions as six Gaussian bands (see dashed lines in Figure 6) where each band consists of a peak center (transition energy), width, and integrated intensity. To constrain the simultaneous Gaussian fit of our model, we assumed the energy of the transitions did not change between the RT ABS, LT ABS, and MCD spectra, but allowed the width and integrated intensity of each band to vary freely. The near-IR bands 1–4 of the RT ABS and MCD spectra were simultaneously fit. In the LT ABS spectrum (Figure 6B), these features were detected with substantial noise and were not considered in the fit. Separately, the near-UV bands 5–6 of the RT ABS, LT ABS, and MCD spectra were simultaneously fit. Fitting parameters are summarized in Table S2. We found $\lambda_{max}$ at 5200 cm$^{-1}$, 7050 cm$^{-1}$, 9400 cm$^{-1}$, 11 800 cm$^{-1}$, 23 200 cm$^{-1}$, and 26 100 cm$^{-1}$ for bands 1–6, respectively. Significant figures in the near-IR region are based on a less than 100 cm$^{-1}$ measurement step size below 12 500 cm$^{-1}$ and on a less than 50 cm$^{-1}$ step size below 8000 cm$^{-1}$. Significant figures in the near-UV region are based on a less than 200 cm$^{-1}$ measurement step size.

Several factors allow assignment of bands 1–4 as d → d in character and bands 5–6 as trifluoroethoxide to copper charge.
transferred (CT) in character. First, bands 1–4 in the RT ABS are low intensity ($\epsilon < 300 \text{ M}^{-1} \text{ cm}^{-1}$) compared to bands 5–6. In transition metal complexes with incompletely filled d orbitals, low intensity features are usually the electric dipole forbidden d $\rightarrow$ d transitions. In contrast, the high intensity bands 5–6 are likely electric dipole allowed transitions such as from a ligand p orbital to a copper d orbital. Next, the relative intensities of the features in the RT ABS and MCD spectra suggest the near-IR transitions are predominantly d $\rightarrow$ d in character.31,32 As shown in Figure S8, the intensity of all transitions in the MCD spectrum are temperature dependent indicating they are all C-term features. In low-symmetry sites, where all the electronic states are expected to be nondegenerate, C-term intensity is driven by spin–orbit coupling. The spin–orbit coupling is larger for copper than the ligand atoms ($\xi_{\text{Cu}} = 830 \text{ cm}^{-1}$, $\xi_{\text{O,N}} \approx 150$, 76 cm$^{-1}$ for the free ions).29 The magnitudes of intensities of copper-based d $\rightarrow$ d transitions are expected to increase relative to CT transitions when going from the RT ABS to the MCD spectrum. The ratio $C_{\text{p}}/D_{\text{p}}$ is commonly used to make this comparison between the C-term intensity (MCD), $C_{\text{p}}$, and the dipole transition strength (RT ABS), $D_{\text{p}}$, for each band.33–35 Here, we use peak intensity maxima from the Gaussian fits to approximate $C_{\text{p}}/D_{\text{p}}$ ratios as MCD/RT ABS ratios for bands 1–6. The MCD/RT ABS ratios are larger in magnitude for bands 1–4 (MCD/RT ABS = 0.076 $\times 10^{-3}$, 0.16 $\times 10^{-3}$, $-0.053 \times 10^{-3}$, and $-0.12 \times 10^{-3}$ respectively) compared to bands 5–6 (MCD/RT ABS = $-0.009 \times 10^{-3}$ and $-0.02 \times 10^{-3}$ respectively), which supports the assignment of the low energy peaks as transitions within the d manifold.

Finally, the presence of the CT transition in CuI$^-$–O(TFE) but not in the precursor Tp$^{6+}$CuI$^-$(OTf$_2$) suggests the trifluoroethoxide ligand as the donor primarily responsible for bands 5–6 and the red color of CuI$^-$–O(TFE). Bands 5 and 6 are rationalized as transitions from two lone-pair orbitals O(TFE) $\pi_2$ and O(TFE) $\pi_{\sigma}$, named for their $\pi$ and $\sigma$ bonding orientation relative to the Cu–O bond, respectively. The $\sigma$ bond to copper is expected to be stabilized in energy relative to the $\pi$ bond to copper, making O(TFE) $\pi_{\sigma}$ $\rightarrow$ Cu $d_{x^2-y^2}$ the higher energy transition, band 6. Additionally, we calculate the experimental oscillator strength $f_{\text{exp}} = 4.61 \times 10^{-4} \epsilon_{\text{m}} v_{\text{RT ABS}}$ from the RT ABS maximum $\epsilon_{\text{m}}$ and the full width at half-maximum $v_{\text{RT ABS}}$ using the Gaussian fit parameters for bands 5–6 in Table S2. The oscillator strength of these transitions roughly correlates with the overlap of the donor orbitals (O(TFE) $\pi_2$ and O(TFE) $\pi_{\sigma}$) and acceptor orbital Cu $d_{x^2-y^2}$ in the charge transfer transition and is used in the discussion section below.

Bands 1–4 are due to transitions from the four fully occupied copper-based d orbitals to the singly occupied copper based $d_{x^2-y^2}$ orbital. We can assign the identity of each transition based on the literature assignments for CuI$^-$ compounds in distorted tetrahedral environments. From lowest to highest energy (bands 1–4) the assignments are usually $d_{x^2}$ $\rightarrow$ $d_{x^2-y^2}$, $d_y$, $d_{y^2}$, $d_{xz}$, and $d_{yz}$ in the charge transfer transition and is used in the discussion section below.36

It is possible to fit the MCD spectrum with five Gaussian bands resulting in $\lambda_{\text{max}}$ at 5010, 7100, 9500, 10 500, and 11 500 cm$^{-1}$ and the sign pattern $+$, $+$, $-$, $-$, $+$, $-$ (Figure S10, Table S3). In this case the transitions are assigned as $d_{x^2-y^2}$ $\rightarrow$ $d_{x^2-y^2}$, N(Pz) $\rightarrow$ $d_{x^2}$, $d_y$ $\rightarrow$ $d_{x^2-y^2}$, $d_{y^2}$, $d_{xz}$, and $d_{yz}$ $\rightarrow$ $d_{x^2-y^2}$ with the sign pattern for the ligand field transitions consistent with the literature. The N(Pz) $\rightarrow$ $d_{x^2-y^2}$ transition has been observed before in a similar CuI$^-$-thiolate complex.33 However, we would expect a dipole allowed N(Pz) $\rightarrow$ $d_{x^2-y^2}$ CT transition to have increased intensity in the RT ABS, which is not observed for CuI$^-$–O(TFE). The discrepancy in the signs of the MCD transitions compared to previous literature leaves the assignment of the ligand field transitions somewhat ambiguous. The implications of this for the electronic structure analysis are discussed below.

Resonance Raman. To further support the assignment of the LMCT transition, we performed resonance Raman ($r$R) spectroscopy on CuI$^-$–O(TFE) and the isotopically labeled CuI$^-$–O(DCM) ($r$R only on the trifluoroethoxide ligand). Spectra were recorded with an incident wavelength of 426 nm (23 474 cm$^{-1}$). In CuI$^-$–O(TFE), three low-energy peaks at 524, 592, and 690 cm$^{-1}$ and two high energy peaks at 1139 and 1274 cm$^{-1}$ were observed (Figure 7A, Table S4A). In CuI$^-$–O(DCM)–$d_2$, the three low energy peaks down-shifted to 521, 567, and 678 cm$^{-1}$, and two high energy peaks at 1008 and 1154 cm$^{-1}$ were observed. In both CuI$^-$–O(TFE) and CuI$^-$–O(DCM)–$d_2$, low intensity features are also observed at very low energies <400 cm$^{-1}$ and are not affected by deuteration of O(TFE). The most intense features in the $r$R spectrum are all affected by deuteration of O(TFE), supporting assignment of the electronic transition at 23 200 cm$^{-1}$ as an O(TFE) $\rightarrow$ Cu $d_{x^2-y^2}$ CT. As such we expect the observed frequencies to
correspond to normal modes involving displacement of copper and the trifluoroethoxide ligand.

First, we will assign the three low-energy features from 500 to 700 cm$^{-1}$. These likely involve the heaviest atoms which indicates that these bands are $\nu$(Cu–O) in character. The peak at 592 cm$^{-1}$ is the most intense indicating it has the most $\nu$(Cu–O) stretch character of the three since these two atoms are involved in the CT. It is also substantially shifted by deuteration ($-25$ cm$^{-1}$) indicating movement of the oxygen atom may drag along the C$fi$O bond, indicating distortions of C$_\beta$–F$_\alpha$. The peak at 690 cm$^{-1}$ involves an intermediate amount of $\nu$(Cu–O) character. However, it is also substantially shifted by deuteration ($-12$ cm$^{-1}$), indicating movement of the C$_\alpha$O$_\beta$ bond. The peak at 592 cm$^{-1}$ with the most $\nu$(Cu–O) stretch character constitutes one of the few known Cu$II$-alkoxide stretch frequencies.

In support of our interpretation, we note Cu$II$ proteins and small molecule complexes in similar distorted tetrahedral environments exhibit similarly complicated Cu-ligand stretching patterns. Plastocyanin, a type 1 blue copper protein, has multiple Cu–S stretching frequencies between 350 and 500 cm$^{-1}$.

Figure 7. (A) Room temperature resonance Raman spectra of Cu$II$–O(TFE) (blue) and Cu$II$–O(TFE)–d$_1$ (red) in DCM with an incident wavelength of 426 nm, exciting the O(TFE) $\rightarrow$ Cu d$_{3c}$ transition. Vibrational frequencies of Cu$II$–O(TFE) are labeled in blue and the shifts upon isotopic labeling are listed in black. The peak in Cu$II$–O(TFE)–d$_1$ that lies under a DCM solvent peak is labeled with a star. (B) Calculated resonance Raman spectra of the optimized structure of Cu$II$–O(TFE) (blue) and Cu$II$–O(TFE)–d$_2$ (red). The dominant motions associated with each normal mode are labeled. Shifts upon isotopic labeling are listed for normal modes that closely correspond in Cu$II$–O(TFE) and Cu$II$–O(TFE)–d$_2$.

Next, we will assign the features in the high-energy region above 1000 cm$^{-1}$, where we expect normal modes based on the O(TFE) ligand with little movement of the heavy copper atom. We suggest two interpretations of the data in this region. First, the peaks at 1139 and 1274 cm$^{-1}$ for Cu$II$–O(TFE) can be assigned as dominantly $\nu$(C–O) and w(C–H), respectively, based on the expected frequencies of these modes from IR and Raman spectroscopy ($\approx$1090 cm$^{-1}$ for $\nu$(C–O) and 1140–1400 cm$^{-1}$ for w(C–H)).$^{34}$ In Cu$II$–O(TFE)–d$_2$, a w(C–D) is expected to appear at much lower frequency and is assigned as the peak at 1008 cm$^{-1}$. Deuteration of the α-C–H is expected to slightly raise $\nu$(C–O) (see calculations). We tentatively assign the low intensity peak at 1154 cm$^{-1}$ to $\nu$(C–O); however, a DCM solvent peak appears at this frequency, which obscures the assignment.

In a second possible interpretation, the high-energy peaks in Cu$II$–O(TFE) may be assigned as a Fermi resonance between a w(C–H) mode and the first overtone of the peak at 592 cm$^{-1}$ (expected to appear at 1184 cm$^{-1}$). The Fermi resonance red shifts the overtone peak by $-45$ cm$^{-1}$ so it appears at 1139 cm$^{-1}$. An equivalent blue shift of the w(C–H) up to 1274 cm$^{-1}$ means the true w(C–H) is expected to appear at $\approx$1229 cm$^{-1}$. In Cu$II$–O(TFE)–d$_2$, a significant red shift of the w(C–D) would inactivate the Fermi resonance coupling and lead to one w(C–D) at 1008 cm$^{-1}$ with double the intensity of the peaks in Cu$II$–O(TFE). DFT calculations (see below) support the first interpretation presented, but due to the solvent background, assignments remain uncertain.

Overall, our rR data confirm the assignment of the LMCT as predominantly O(TFE) p$_x$ $\rightarrow$ Cu d$_{3c}$ in character. The main $\nu$(Cu–O) stretch at 592 cm$^{-1}$ indicates that the Cu–O bond is softer than in a comparable Cu-peroxo compound with $\nu$(Cu–O) of 645 cm$^{-1}$. Deuteration of the α-C–H is expected to slightly raise $\nu$(C–O) (see calculations). We tentatively assign the low intensity peak at 1154 cm$^{-1}$ to $\nu$(C–O); however, a DCM solvent peak appears at this frequency, which obscures the assignment.

Quantum Chemistry. To support our analysis, we performed DFT and TDDFT calculations. An all-atom geometry optimization of Cu$II$–O(TFE) was initiated from the geometry determined by X-ray crystallography.$^{21}$ The atomic coordinates and most relevant structural features are compared in the Supporting Information (Section 5b, Figure S13). Between the crystal structure and the optimized geometry, the long Cu–N$_{4a}$ bond (2.2270(11) vs 2.26 (Å)), the Cu–O bond length (1.8324(10) vs 1.87 (Å)), and the large Cu–O–C angle (135.48(9)$^\circ$ vs 134)$^\circ$ were maintained, respectively. The optimized geometry was used in all further calculations.

EPR property calculations support the interpretation of the experimental EPR data. Calculated Mulliken spin populations of $\approx8\%$ on each of the two basal nitrogen atoms agree with the experimental spin populations derived from $^{14}$N ENDOR (see calculations). The hyperfine coupling values of the basal nitrogen atoms are in reasonable agreement with the values determined from simulation of the $^{14}$N ENDOR (compare Table S1D and S1E). However, the calculation predicts about 60% spin population on copper and 23% spin population on the trifluoroethoxide oxygen, which is larger than the experimental upper bound for $\sigma_o$ of $\approx0.03\%$ in a single crystal ($\approx15(3)\%$ in solution). Also, DFT predicts hyperfine couplings for the trifluoroethoxide protons that are larger than...
observed. Overall, this suggests DFT overdelocalizes the spin density and overestimates the radical character on the trifluoroethoxide ligand. The DFT-predicted copper hyperfine coupling and g values are in poor agreement with experiment. Correct modeling of the electron correlation and the covalency of CuII-ligand bonds is essential for accurate g shift predictions. Multiple approaches have been used to improve EPR property calculations in related systems, although these were not pursued here.44,45

DFT calculations support the assignment of the experimental rR shifts. Calculations were performed on CuII–O(TFE) and CuII–O(TFE)-d2. Calculation of resonant enhancement of vibrational modes predicts three vibrations enhanced between 400 and 700 cm$^{-1}$ (Figure 7B, Table S4A). Dominantly, the modes are ν(Cu–O) + δ(F–C$_{2}$–F), ν(Cu–O), and ν(Cu–O) + δ(O–C–C$_{p}$) at 497, 553, and 663 cm$^{-1}$. In CuII–O(TFE)-d$_{2}$, three peaks with nearly identical normal modes are downshifted by -1, -20, and -13 cm$^{-1}$, respectively. This is in reasonable agreement with the experimental isotopic shifts of -3, -25, and -12 cm$^{-1}$ allowing more definitive assignment of the rough experimental mode assignments described above.

To higher energy, the rR calculation for CuII–O(TFE) predicts enhancement of a nearly pure ν(C–O) at 1094 cm$^{-1}$. The calculation for CuII–O(TFE)-d$_{2}$ predicts enhancement of two vibrational modes involving ν(C–O); ν(C–O) + ν(C$_{p}$–F) at 1086 cm$^{-1}$ and ν(C–O) + w(C–D) at 1125 cm$^{-1}$. The latter is isotopically shifted +30 cm$^{-1}$ from the calculated ν(C–O) for CuII–O(TFE). This is in reasonable agreement with the experimental isotopic shift of +15 cm$^{-1}$ for the features at 1139 and 1154 cm$^{-1}$ in CuII–O(TFE) and CuII–O(TFE)-d$_{2}$, respectively.

The experimental feature we assign as w(C–H) at 1274 cm$^{-1}$ in CuII–O(TFE) is not enhanced in the calculation. A numerical Raman calculation for CuII–O(TFE) (SI section 3.c) predicts that a ν(C–C$_{p}$) + w(C–H) mode at 1217 cm$^{-1}$ and a w(C–H) mode at 1359 cm$^{-1}$ will have Raman activity (appearing unenhanced at 1215 and 1353 cm$^{-1}$ in the analytical rR calculation). However, the calculation for CuII–O(TFE)-d$_{2}$ does predict enhancement of the w(C–D) mode at 964 cm$^{-1}$, isotopically shifted by -251 cm$^{-1}$ and -389 cm$^{-1}$ from the ν(C–C$_{p}$) + w(C–H) and w(C–H) in CuII–O(TFE), respectively. The former is in closer agreement with the experimental isotopic shift of -266 cm$^{-1}$ from 1274 to 1008 cm$^{-1}$. Given this similar isotopic shift between calculation and experiment, these experimental modes likely involve a w(C–H) and w(C–D), respectively.

Figure 8 shows a selection of DFT-calculated molecular orbitals, spin populations and transition difference densities. The β-LUMO (Figure 8A) and the spin density distribution (Figure 8B) support our selection of nuclei used in the distributed point-dipole approximation. As will be discussed below, the calculated β-LUMO also supports the orientation of the d$_{π}$–β– orbital such that the lobes are nearly bisected by the Cu–O(TFE) bond. In Figure 8C, the TDDFT-predicted transition difference densities are shown for two O(TFE) p → Cu d$_{π}$–β– transitions that make up the intense near-UV absorption band. The calculation incorrectly predicted the energy order of these two transitions so the images are used only to illustrate the orientation of the O(TFE) p orbitals as discussed below (TDDFT discussion in SI section S.a).

### DISCUSSION

With our spectroscopic results, we characterized the electronic structure of this CuII-alkoxide complex. Below we examine the ligand field equations for a d$^{9}$ transition metal in a d$^{6}$ ground state to ascertain the physical origin of the unique EPR parameters. To understand the spectroscopic features engendered by the trifluoroethoxide ligand, we will compare the CuII-alkoxide to well-characterized small molecule CuII-thiolate (CuII–SR) and CuII-alkyloxo (CuII–OOR) complexes in nearly identical geometries (see Table S5 for structural comparison)$^{40,47}$ These complexes exhibit similar EPR spectra, in particular the small CuII-A$_{2g}$ hyperfine coupling. However, in contrast to the near-UV LMCT transition of CuII–O(TFE), the LMCT transitions (from thiolate and alkyloxido ligand donors) in both of these complexes are in the near-IR region, which imparts a blue color to the compounds (see Tables 1 and S1).

### Table 1. Spectroscopic Comparison of CuII–X Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\xi_{\text{OR}}$ (%)</th>
<th>$\Delta E_{2\text{d}}$ cm$^{-1}$</th>
<th>% spin on Cu$^{2+}$</th>
<th>$f_{\text{exp}}$ or $f_{\text{calc}}$ / $f_{\text{norm}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OR</td>
<td>2.44</td>
<td>7050</td>
<td>68$^{a}$ (60)</td>
<td>40 x 10$^{-4}$</td>
</tr>
<tr>
<td>OOR$^{4}$</td>
<td>2.316</td>
<td>8050</td>
<td>62$^{b}$ (52)</td>
<td>55 x 10$^{-4}$</td>
</tr>
<tr>
<td>SR$^{3,46}$</td>
<td>2.23</td>
<td>9250</td>
<td>36$^{c}$ (34)</td>
<td>74 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

$^{a}$In parentheses are results from DFT (B3LYP for or OR, OOR) calculations.$^{b}$From hyperfine coupling of remote nuclei.$^{c}$From EPR g values and INDO/S–CI calculations.$^{d}$From Cu-L edge XAS results.$^{e}$Ratio of oscillator strengths of $\sim$σ and π LMCT transitions.
large gzz and NIR MCD Transitions. The origins of the unusually large gzz in CuII-O(TFE) can be rationalized via a ligand field theory argument for a d9 transition metal in the d⊥⊥ ground state.39 Assuming the simplified case of an axial g tensor, the gzz value can be approximated as

\[ \Delta gzz = gzz = \frac{\alpha^2}{e^{\gamma^2} + e^\gamma} = \frac{\Delta E}{\Delta E_L} \]

Here \( \xi \) is the one-electron spin–orbit coupling constant (830 cm\(^{-1}\) for the free CuII ion). The coefficients \( \alpha^\gamma \) and \( \alpha^\delta \) quantify the d⊥⊥ and d∥ character of the ground state and excited state, respectively. Larger \( \alpha^\gamma \) indicates increased d orbital character. \( \Delta E_L = E_\gamma - E_\delta \) is the transition energy for promoting one electron from the doubly occupied dyy Cu-based molecular orbital (MO) to the d∥ orbitals Cu-based singly occupied MO (SOMO).

\( \Delta E_L \) can be estimated from eq 3 by comparison to the allylperoxo complex, CuIII-OOR, using

\[ \Delta E_{L,CuOOR} = \Delta E_{L,CuOOR} = \frac{\Delta g_{CuOOR}}{\Delta g_{CuOOR}} \]

(4)

with \( \Delta g_{CuOOR} = 0.316 \) and \( \Delta E_{L,CuOOR} = 8050 \text{ cm}^{-1} \) (Table 1)34 and \( \Delta g_{CuOOR} = 0.437 \). As ground-state DFT (B3LYP) predicts more spin-polarization on copper in CuII-O(TFE) (60%) versus CuII-OOR (52%),34 we expect increased copper character in the ground state and consequently larger \( \alpha^\gamma \) in the CuII-alkoxide, and therefore \( \Delta g_{CuOOR} < \Delta g_{CuOOR} \). With this, eq 4 yields \( \Delta E_{L,CuOOR} > 5821 \text{ cm}^{-1} \) and we can assign the peak at 7050 cm\(^{-1}\) (band 2 in Figure 6C) to the dyy → d∥ transition. We assign the other three transitions in the near-IR region based on the expected energy order of the d orbitals in a distorted tetrahedral environment. Namely, we support the four-Gaussian model described in the Results section and assign band 1 (5200 cm\(^{-1}\)) to dzx → d∥, band 2 (9400 cm\(^{-1}\)) to dyy → d∥, and band 3 (4150 cm\(^{-1}\)) to d∥ → d∥. As noted above, the signs of the MCD transitions differ from expectations based on the literature, but predicting signs can be challenging.31,32 The small transition energy \( E_\gamma - E_\delta \) is the principal reason for the large gzz.

Small \( \Delta A_{zz} \). The hyperfine coupling can be derived from ligand field theory assuming a simplified axial hyperfine tensor with \( \Delta A_{zz} = A_q \) where

\[ A_q = \gamma_0 \left[ -\alpha^2 \gamma_0 - \frac{4}{7} \alpha^2 \gamma_0 + \frac{3}{7} (g_\sigma - g_\pi) + (g_\pi - g_\sigma) \right] \]

(5)

\( \gamma_q \) is a quasistatic parameter that depends on the nucleus and is typically given the value \( \approx 400 \times 10^{-4} \text{ cm}^{-1} \) for copper. \( \gamma_q \) is a unitless parameter which represents the isotropic hyperfine coupling of the copper nucleus with a typical upper bound value of 0.43.29

The difference in sign of terms one and two compared to terms three and four in eq 5 means a small \( A_q \) can be a result of cancellation of terms. Noting \( g_\pi \approx 2.09 \) in both CuII-O(TFE) and CuII-OOR, one can simplify eq 5 to \( A_q = P_q (-C + \Delta g_\parallel) \) and estimate a parameter \( C_{CuOOR} \) for CuII-OOR from the literature \( \Delta g_\parallel \) value (Table 1). Using \( C_{CuOOR} < C_{CuOOR} \), this predicts copper hyperfine coupling for CuII-O(TFE) of \( \Delta A_{zz} = 316 \text{ cm}^{-1} \), close to the experimental value of \( 40 \times 10^{-4} \text{ cm}^{-1} \). This again implies \( C_{CuOOR}/C_{CuOOR} > 1 \), which indicates larger \( \alpha^\gamma \) and increased copper character in the ground state of the alkoxide complex. This analysis depends on the sign of the hyperfine coupling being the same in both cases (here assumed positive). The small \( \Delta A_{zz} \) is a result of the large gzz value (term 4 in eq 5, driven by the small transition energy \( E_\gamma - E_\delta \) and the large spin population on copper (terms 1 and 2 in eq 5, driven by \( \sigma_\parallel \) ≥ 68%) canceling terms in eq 5.

Nature of the Cu-II(O-TFE) Bond. From single crystal EPR, we found the LMCT acceptor orbital (d∥) is oriented such that the lobes are in a plane approximately perpendicular to the Cu–Naxial bond. From resonance Raman and MCD spectroscopies, we know that the LMCT transition in the room temperature absorption spectrum has two components at 26 100 and 23 200 cm\(^{-1}\) originating from the donor O(TFE) pπ and O(TFE) pπ orbitals, respectively. The orientations of the pseudo-σ and pπ orbitals relative to the Cu–O bond are illustrated by the transition difference densities in Figure 8C.

In the thiolate- and allylperoxo-ligated CuII complexes, the LMCT transition is similarly comprised of two transitions from p orbitals. These are termed \( p_\sigma \) and \( p_\pi \) in CuII–SR and CuII–OOR due to their orientation with respect to the Cu-X(CT donor) bond.33,34 The transition from the donor orbital with \( \pi \) orientation appears to lower energy in both cases, and the \( p_\sigma \) transition relative to the pseudo-σ transition is rationalized as a rotation of the d∥ acceptor orbital so that its lobes are bisected by the Cu–X bond. This allows for excellent overlap of the LMCT donor orbital with \( \pi \) orientation with the copper d∥ acceptor orbital.

Similarly, in CuII–O(TFE), the oscillator strength of the lower-energy O(TFE) pπ → Cu d∥ transition is larger (\( f_{oexp} = 0.051 \)) than for the O(TFE) pπ → Cu d∥ transition (\( f_{oexp} = 0.038 \)). This is evidence that the d∥ orbital lies such that its lobes are bisected by the Cu–O bond (Figure 8A) and indicates a dominantly \( \pi \) bonding interaction. However, the ratios of the oscillator strengths \( f_{oexp}/f_{oexp} \) for CuII–SR, CuII–OOR, and CuII–SR (0.003 < 0.161 < 0.735, respectively, Table 1) show an increase in the relative overlap of the pπ donor compared to the pπ donor with the Cu d∥ acceptor. This ratio trend is due predominantly to a larger oscillator strength for the pπ → Cu d∥ transition in CuII–O(TFE) (see Table S6).

The increase in relative intensity of the O(TFE) pπ → Cu d∥ transition in CuII–O(TFE) may indicate increased \( \sigma \) bonding character compared to the CuII–altlylperoxo and CuII thiolate. In a molecular orbital approach, we expect a bonding and antibonding combination of MOs to form between O(TFE) pπ and d∥, where the bonding orbital is dominantly O(TFE) π pπ and the antibonding is dominantly d∥. The \( \pi \) bond results in an analogous set of bonding and antibonding MOs formed between O(TFE) pπ and d∥ (see Figure 9).

The bonding MO formed by the O(TFE) pπ/d∥ interaction will have increased metal character as the \( \sigma \) bonding interaction becomes stronger. An increase in metal character of the O(TFE) pπ donor orbital will increase overlap with the acceptor d∥ orbital and result in the large integrated area of
The O(TFE) p Loan → Cu d Loan transition that we observed in this work.

An increase in the σ bonding interaction would also raise the energy of the d Loan antibonding orbital closer to the d Loan antibonding orbital, as illustrated in Figure 9. This is consistent with the small transition energy E Loan → σ* that drives the large shift in g Loan for CuII–O(TFE) (relative to g Loan = 2.21 and 2.316 for CuII–SR and CuII–OOR, respectively).

Origin of Near-UV Charge Transfer. The red color (LMCT at 420 nm, 23 800 cm−1) of the CuII–alkoxide is notably different from the blue color of CuII–alkylperoxo and CuII–thiolate complexes (LMCT at 600 nm, 16 600 cm−1). This is a consequence of the nature of the trifluoroethoxide CT donor. The increased transition energy for an alkoxide donor is expected based on the increase in ionization energy for an alcohol compared to an alkylperoxide or thiol (10.48 > 9.36 > 9.31 eV for ethanol, n-butylperoxide, and ethanethiol, respectively).

The increased ionization energy for alcohols compared to peroxides comes in part from the nature of the molecular orbitals formed between the O–Cσ bond in an alkoxide versus the O–O bond in a peroxide. The highest occupied MOs in an alkoxide are oxygen nonbonding orbitals, whereas in an alkylperoxide, they are destabilized π* antibonding orbitals. In addition, the trifluoromethyl group is strongly electron withdrawing, further increasing the ionization energy of the trifluoroethoxide ligand (11.49 eV for trifluoroethanol) compared to a nonhalogenated alcohol.

Comparison with Copper Sites in Biology. CuII–O(TFE) shares a small hyperfine coupling CσAox, with some members of the family of type 1 copper proteins. The type 1 blue copper site in plastocyanin (extensively reviewed by Solomon) is a distorted tetrahedral CuII site in a d Loan ground state, which leads to an axial EPR spectrum. Plastocyanin is often described as possessing a uniquely small CuAox hyperfine coupling (g Loan = 2.23, CσAox = 6.3 × 10−4 cm−1) compared to type 2 or “normal” copper sites such as D4h [CuCl2]4− (g Loan = 2.22, CσAox = 164 × 10−4 cm−1). A highly covalent Cu–S(Cys) bond decreases the spin density on the copper nucleus and leads to small CuAox hyperfine coupling (decrease of terms 1 and 2 in eq 5). In contrast, in CuII–O(TFE) we have found significant spin density on the copper nucleus of ≈68%. The resulting increase in magnitude of the contact and spin-dipolar contributions (terms 1 and 2) to the hyperfine coupling is offset by the increased g Loan-dependent orbital contribution (term 4) of opposite sign, which is due to the small transition energy E Loan → σ*. Overall, this cancellation of terms in eq 5 drives the small CuAox.
density on copper), indicating a more ionic Cu–O bond in CuII−O(TFE), relative to the comparable CuII-alkylperoxo (≈62% spin density on copper) and CuII-thiolate complexes (≈40% spin density on copper).33,50 The αC–H bond strength of an alcohol is known to depend on the hydroxyl group protonation state. It has been predicted that with ionic counterions, such as Na+ and K+, the αC–H bonds in methanol are weakened from ≈91 kcal/mol to ≈81 kcal/mol and ≈79 kcal/mol, respectively.11 Similarly, the αC–D stretching frequency (which is roughly proportional to bond strength)51 in trifluoroethanol-d2 has been observed to decrease upon deprotonation with NaOH.32 We expect the ionic interaction between CuII and the trifluoroethoxide in CuII−O(TFE) to weaken the αC–H bond strength based on these findings from the literature. However, in a separate reactivity study, it was found that oxidation of the O(TFE) ligand with external oxyl radical hydrogen atom acceptors is not facile, indicating that the activation of the αC–H bond is not significant enough to promote bond cleavage in this system.21

### CONCLUSION

In this study we have characterized in detail the electronic structure of a CuII-alkoxide complex as a model structural intermediate in copper-catalyzed alcohol oxidation. EPR spectra reveal the orientation of the dxy−dxy SOMO with lobes bisected by the Cu−O bond. MCD and resonance Raman spectra show the donor in the LMCT transition is dominantly the O(TFE) ligand. The increased contribution from the O(TFE) p−σ donor in the LMCT transition indicates both σ and π bonding interactions are present, relative to CuII-thiolate and CuII-alkylperoxo bonds. This increased ratio of σ/π bonding character reduces the energy of the dxy → dxy−dxy transition. This small transition energy drives a large shift in gπ and, together with small spin delocalization, contributes to the small hyperfine coupling 1D A1C. Single-crystal and solution ENDOR spectra, analyzed using a distributed point-dipole model, suggest the unpaired electron is highly localized on the copper atom with ≤15% spin density on oxygen of the alkoxide ligand. A ligand field analysis using EPR and MCD data indicates substantial copper character in the ground state SOMO relative to related CuII-alkylperoxo and CuII-thiolate systems in nearly identical pyrazolyl ligand scaffolds. However, this relatively ionic bond does not sufficiently modulate the αC–H bond to promote ligand oxidation.21 This model complex serves as one of the only CuII-alkoxide complexes spectroscopically characterized to this extent. This insight lays the basis for further elucidating the mechanism of Cu-mediated alcohol oxidations.

### EXPERIMENTAL SECTION

**Synthesis and Characterization.** Tp′′′′Cu′II(OC1H3CF3) and Tp′′′′Cu′II(OCD1C1F4) were synthesized as previously described and the structure of Tp′′′′Cu′II(OC1H3CF3) was determined previously.31 Tp′′′′Cu′II(OCD1C1F4) was used to assign hyperfine couplings of the αC–H protons of the trifluoroethoxide ligand and to assign vibrational modes in the resonance Raman spectra. Tp′′′′ZnII(OC1H3CF3) was prepared through an analogous synthetic route. Tp′′′′Cu′II(OC1H3CF3) and Tp′′′′ZnII(OC1H3CF3) crystallize in the same space group (P21/n) with nearly identical unit cell dimensions (see SI section 6a). All samples for spectroscopy were prepared in a nitrogen filled glovebox using deoxygenated and water-free solvents.53

**Single-Crystal 34 GHz EPR and ENDOR.** Single crystals of Tp′′′′ZnII(OC1H3CF3) doped with Tp′′′′Cu′II(OC1H3CF3) were grown from a concentrated pentane solution containing a ≈1:99 ratio of CuII-Zn complexes at −30 °C. The exact percentage of Cu incorporation was not determined.

A single crystal was loaded into a 1 mm O.D. quartz capillary EPR sample tube and sealed in place with vacuum grease. A goniometer was mounted on to the sample rod and EPR sample tubes were placed into a Bruker EleXsys E880 X/Q spectrometer such that the long axis of the capillary was perpendicular to the direction of the magnetic field. The sample was rotated around the capillary axis (sample rod axis) in 15° increments from 0° to 180°. The orientation of the crystal relative to this rotation axis was determined by X-ray crystallography after recording EPR and ENDOR data.

At each rotation increment, a pulse field-swept EPR spectrum and a Davies ENDOR spectrum were recorded. All single-crystal measurements were carried out in a Bruker EN 5107D2 resonator at ≈34 GHz held at 10 K with an Oxford CF9350 liquid helium cryostat and ITCS90S temperature controller. Pulse field-swept EPR spectra were FID detected following a 1 μs pulse. The Davies ENDOR spectra were Hahn echo detected (π−T−π−2−t−r−π−t−r−π−r−t−r−e−e) with pulse lengths and timings given in specific figure captions. During time T, the RF pulse was applied. Microwave frequencies were measured with the built-in frequency counter, and accurate magnetic field values were obtained using a teslameter.

The above was repeated for a second single crystal. Data are shown in the electronic Supporting Information (section 1).

**Frozen Solution 9.2 and 34 GHz EPR and ENDOR.** The continuous-wave (CW) EPR spectrum at 9.2 GHz, reported previously, was recorded on a Bruker EMX spectrometer in an SHQF resonator at 120 K in a frozen glass of ≈3 mM Tp′′′′Cu′II(OC1H3CF3) in toluene.32 The field axis was corrected for a 0.5 mT difference between nominal and teslameter-determined field values.

For pulse field-swept 34 GHz EPR spectroscopy, a 1.5 mM solution of Tp′′′′Cu′II(OC1H3CF3) in 1:1 DCM:toluene was flash frozen in a 1 mm O.D. quartz EPR sample tube. Pulse field-swept and Davies ENDOR spectra were recorded in the same spectrometer and resonator as described above at 10 K. The field-swept spectrum was Hahn echo detected (π−T−π−2−r−t−r−e−e−e). Davies ENDOR was echo detected (π−T−π−2−r−t−r−e−e−e) with pulse lengths and timings given in the figure captions. Microwave frequencies were measured with the built-in frequency counter. Magnetic field values were corrected for a 1.5 mT shift between nominal and teslameter-determined field values.

**Electronic Absorption and Magnetic Circular Dichroism.** The UV–vis spectrum was acquired previously and recorded with a 2 nm step size.21 The near-IR/IR spectrum was collected using an Agilent Cary 5000 spectrophotometer with a 1 cm path length. MCD spectra were prepared by saturating a pentane:toluene (9:1) solution with Tp′′′′Cu′II(OC1H3CF3). To this, a drop of paratone oil was added to increase the viscosity. The solution was pipetted dropwise onto a quartz disk and the solvent was allowed to evaporate, creating a thin film. Several layers of Tp′′′′Cu′II(OC1H3CF3) were deposited in this way and the film then sandwiched with a second quartz disk. The thin film sample was briefly exposed to atmosphere while mounting into the MCD sample rod which was then placed in a liquid helium cooled variable temperature, superconducting magnetooptical cryostat (Cryo-Industries SMC-1659 OVT) with the sample compartment oriented in the Faraday configuration. Absorption and MCD spectra were collected simultaneously using an Aviv 40 DS spectropolarimeter equipped with an additional InGaAs (Teledyne Judson) detector for detection down to 5000 cm−1 (2000 nm). Variable temperature, variable field measurements were carried out at 5, 10, 20, and 40 K with the magnetic field varied from 0 to 6 T in 1 T steps at each temperature. Data was collected with a 2 nm step size from 370 to 860 nm and a 5 nm step size from 800 to 2000 nm. At 5 K, the sample was screened for depolarization by matching the CD spectra of a chiral molecule placed before and after the sample. Depolarization was less than 10%. The differential absorption of the MCD experiment is defined as ΔA = A1 − A0, where A1 and A0 refer to the absorption of left and right circularly polarized photons in the sign convention of Piepoh and Schatz.54

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Spectra were modeled using a sum of Gaussians defined in the Matlab program. The models were simultaneously fit to the data (using the assumptions presented in the Results section) using the least-squares fitting algorithms implemented in EasySpin.55

**Resonance Raman.** Resonance Raman samples were prepared by dissolving TP60Cu60(OCH2CF3) to an optical density of 2 at 420 nm (1.38 mM) in DCM. The same was done for the deuterated TP60Cu60(OCD;CF3). These solutions were deposited in 5 mm OD NMR tubes and sealed with electrical tape before removing from the inert atmosphere glovebox.

The 426 nm Raman excitation beam was obtained from the frequency-doubled output of a titanium-sapphire laser (16 ns pulse, 5 μJ/pulse) pumped by a Q-switched (1 kHz), intracavity frequency-doubled Nd:YLF laser (Photonics Industries International). Excitation light was focused through a spherical lens onto the surface of the spinning sample tube, and backscattered (135°) light was collected and collimated with a camera lens and focused with a second lens onto the 0.200 mm entrance slit of a 0.8 m spectrometer (Spex 1401) equipped with a liquid N2-cooled charge-coupled device detector onto the 0.200 mm entrance slit of a 0.8 m spectrometer (Spex 1401) equipped with a liquid N2-cooled charge-coupled device detector (Roper Scientific). A 430 nm-cut notch filter (angle tuned) was placed at the slit to minimize the spectral contribution of Rayleigh scattering. The samples showed no signs of photodegradation after 15 min of continuous laser irradiation. Samples showed decay of rR signal and color after more than 5 h out of the glovebox (data not shown).

Experimental data shown here were collected in less than 3 h.

**EPR Simulations.** All EPR and ENDOR simulations were performed using EasySpin S0.55 For simulation of EPR spectra, the various frames were defined as follows. For P21/n symmetry (space group 14), the crystal frame C (principal axes xC, yC, zC) was defined with zC along the crystal b axis, zL along the crystal c axis, and xC along the a* axis normal to the bc plane of the crystal. The laboratory frame L (xL, yL, zL) was defined with zL along the static field and yL along the axis of single crystal rotation (sample tube long axis).

To determine the orientation of the crystal in the EPR spectrometer, X-ray diffraction was recorded for the single crystal within the EPR tube (identical instrument described in SI section 6). Using the previously solved crystal structure, the rotation axis of crystal sample 1 (presented in article) was found to be along the (0, −3, 4) crystal direction in abc coordinates with 3° accuracy. The rotation axis of crystal sample 2 (presented in SI) was found to be along the (−7, −4, 5) direction in abc coordinates with 2° accuracy.

The molecular frame M (principal axes xM, yM, zM) defined with zM along the Cu−Namide bond and yM perpendicular to zM within the Namide−Cu−O plane such that it points in the direction of the Cu−O bond. The initial g tensor frame before least-squares fitting was taken as collinear with the molecular frame. The copper hyperfine frame was assumed to be collinear with the g frame in all simulations.

With the above frame definitions, the starting orientation (azimuthal angle ϕ), of the crystal in the laboratory xLzL plane and the three Euler angles relating the g tensor frame to the molecular frame remained unknown, for a total of four variables. These variables were determined by least-squares fitting. In increments of 3°, ϕ was varied, followed by a simultaneous least-squares fit of the Euler angles of all 13 spectra in Figure 2C using a grid search algorithm implemented in EasySpin. This same procedure was carried out for crystal 2 and yielded a nearly identical set of Euler angles relating the g frame to the molecular frame.

The frequency change of spectra in Figure 2C is due to a small repositioning of the sample along the laboratory yL axis (perpendicular to the field) to optimize sensitivity. This frequency change is negligibly small, but was nevertheless accounted for in the simulations.

Simulations of single-crystal 1H ENDOR spectra used the full hyperfine tensors (calculated using the point dipole approximation) and the full g tensor. The hyperfine frames are visualized in Figure S6B.

Hyperfine frames (xH, yH, zH) for simulation of the 14N and 19F frozen-solution ENDOR spectra were defined using the crystal structure coordinates. For each nucleus, its zA axis was defined as the unit vector pointing from the nucleus to the copper atom. xH and zA were defined in the plane perpendicular to zA pointing in arbitrary but perpendicular directions. The frames are visualized in Figure S6B.

**Density Functional Theory.** Unrestricted Kohn−Sham (UKS) density functional theory (DFT) calculations were performed with Orca 3.0.2 or 3.0.3.56 Geometry optimization was initiated from the crystal structure coordinates. All atom positions were optimized using the B3LYP60 functional, the Ahlrichs trvp56 basis set, with grid size of 4 and SCF convergence criteria of 1 × 10−6 Eν, Convergence thresholds for the geometry optimization were as follows: energy change 5 × 10−6 Eν, maximum gradient 3 × 10−4 Eν/a0 RMS gradient 1 × 10−6 Eν/a0 maximum displacement 4 × 10−3 a0 and RMS displacement 2 × 10−3 a0.

EPR property calculations of the optimized geometry used the hybrid B3LYP60−62 functional and Barone’s EPR-II basis set.57 The copper atom was modeled with a specialized CF(PPP) basis set to model core polarization.56,60

In preparation for resonance Raman calculations, time-dependent DFT calculations were carried out with the B3LYP functional, the trvp basis set and a grid size of 5.59 The auxiliary basis set tpz/vj was used for the RI approximation for hybrid functionals.60−62 The first 30 excited states were calculated. As solvent models are not available for the resonance Raman calculations in Orca, no solvent model was used. Separate TDDFT calculations using the COSMO69 model for dichloromethane showed little difference in the predicted excited states (data not shown). States 10 and 12 showed O(TFE) p→Cu d*, p→Cu d*, s character, respectively, and were used to predict resonance enhancement of Raman modes.

To obtain a Hessian file for resonance Raman calculations, an analytical frequency calculation was performed using an identical level of theory as for the geometry optimization. Additionally the tpz/vj auxiliary basis set was used for the RI approximation. The SCF was converged to an energy change tolerance of 1 × 10−8 Eν. Resonance enhancements were predicted using the Hessian file from the analytical frequency calculation for excited states 10 and 12 using the same level of theory as for TDDFT calculations. A sample input block is provided in the electronic Supporting Information (section 3b). Resonance Raman calculations for the isotopologue molecule CuII−O(TFE)−d2 were calculated by manually editing the masses of the appropriate hydrogen atoms in the Hessian input file. The new vibrational frequencies for the isotopically labeled molecule were calculated using the standalone orca_vib program. This adjusted Hessian was used in the input block for resonance Raman calculations of CuII−O(TFE)−d2. In both cases, the resonance Raman calculation produced .aux input files which were fed into the orca_as program to produce resonance Raman spectra.

Normal modes were visualized using Avogadro (version 1.0.3)71 Molecular orbitals, spin density, and transition difference densities were visualized using UCSF Chimera (version 1.8).72

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**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b13088.

Crystal data for TpBuZnII(OCH2CF3). (CIF)

Crystal data for TpBuZnII(OCH2CF3). (CIF)

Simulation parameters for EPR and ENDOR spectra, supplemental EPR and ENDOR spectra, supplemental electronic absorption and MCD spectra, structural and spectroscopic properties of CuII complexes in the literature, model molecular orbital diagram, additional details about DFT calculations, synthesis, crystallographic information. (PDF)

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