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Electronic Structure and Reactivity Studies of a Nonsymmetric One-Electron Oxidized Cu^{II} Bis-phenoxide Complex

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Abstract

The tetradentate mixed imino/amino phenoxide ligand (N-(3,5-di-tert-butylsalicylidene)-N'-(2-hydroxyl-3,5-di-tert-butylbenzyl))-trans-1,2-cyclohexanediamine (salalen) was complexed with Cu^{II}, and the resulting Cu complex (**2**) was characterized by a number of experimental techniques and theoretical calculations. Two quasi-reversible redox processes for **2**, as observed by cyclic voltammetry, demonstrated the potential stability of oxidized forms, and also the increased electron-donating ability of the salalen ligand in comparison to the salen analogue. The electronic structure of the one-electron oxidized [**2**]⁺ was then studied in detail, and Cu K-edge X-ray Absorption Spectroscopy (XAS) measurements confirmed a Cu^{II}-phenoxyl radical complex in solution. Subsequent resonance Raman (rR) and variable temperature ¹H NMR studies, coupled with theoretical calculations, showed that [**2**]⁺ is a triplet (*S* = 1) Cu^{II}-phenoxyl radical species, with localization of the radical on the more electron-rich aminophenoxide. Attempted isolation of X-ray quality crystals of [**2**]⁺ afforded [**2H**]⁺, with a protonated phenol bonded to Cu^{II}, and an additional H-bonding interaction with the SbF₆[−] counterion. Stoichiometric reaction of dilute solutions of [**2**]⁺ with benzyl alcohol showed that the complex reacted in a similar manner as the oxidized Cu^{II}-salen analogue, and does not exhibit a substrate-binding pre-equilibrium as observed for the oxidized bisaminophenoxide Cu^{II}-salan derivative.

TOC Image

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1. Introduction

The incorporation of redox-active ligands into transition metal complexes has garnered significant interest,[1–6] drawing inspiration from enzymatic systems. Pro-radical ligands are essential components in the active sites of many metalloenzymes including cytochrome *c* oxidase[7] and P450,[8] glyoxal oxidase,[9] and galactose oxidase (GO_{ase}).[10] The Cu-containing GO_{ase} is the archetypical example, catalyzing the oxidation of primary alcohols to aldehydes with the concomitant reduction of O₂ to H₂O₂. [11, 12] The catalytically active form of GO_{ase} incorporates a Cu^{II} metal center and a tyrosyl ligand radical, which is cross-linked with a cysteine residue, with each undergoing one-electron reduction during substrate oxidation.[10] The simplicity and reactivity of the active site in GO_{ase} has inspired many structural and functional small-molecule models.[13–16]

We, and others, have had a long-standing interest in the electronic structure of oxidized metal salen (salen is a common abbreviation for N₂O₂ bis-imine bis-phenoxide ligands) complexes,[17–44] in particular the similarity of the coordination sphere to GO_{ase}. [15] The highly modular synthesis of salen ligands allows for facile tuning of both steric and electronic properties, and ability to stabilize a wide variety of transition and main group metal complexes in a number of oxidation states.[15, 45–50] Traditionally, the term salen refers to ligands specifically prepared *via* condensation of two equivalents of salicylaldehyde and ethylenediamine, but now includes ligands with different phenyl ring substituents and diamine backbone.[51] The imine functionalities are reducible to afford the corresponding tetrahydrosalen (salan) analogues,[35, 52, 53] while a half-reduced salen ligand (salalen) can be prepared *via* reduction of only single imine function.[54–61] The development of synthetic methodologies for asymmetric salens (ligands with different substitution patterns on each of the phenol moieties) allows for the preparation of a diverse library of ligands.[62]

Upon one-electron oxidation, metal-salen complexes can exhibit redox activity at either the ligand or the metal centre, depending on the transition metal used, the peripheral ligand substituents, the solvent or the temperature. Without the use of *ortho*- and *para*-phenolate protecting groups, oxidized metal salen complexes are prone to rapid polymerization *via* radical coupling even at –80°C.[63–67] In the context of this work, we aimed to study the comparative electronic structure and associated reactivity of the one-electron oxidized forms of Cu salen (**1**), Cu salalen (**2**), and Cu salan (**3**), in which the imine functionalities are reduced sequentially (Figure 1).

We reported previously the one-electron oxidation behavior and reactivity of $[1]^+$, in comparison to $[3]^+$.^[24, 52] Initial studies showed that both oxidized complexes react with the model substrate benzyl alcohol to form benzaldehyde, however compound $[3]^+$ reacts more quickly despite being a weaker oxidant ($E_{1/2}$ of 80 and 450 mV for **3** and **1**, respectively, vs. Fc^+/Fc). A mechanistic difference was uncovered in which initial substrate binding to $[3]^+$ presumably results in more rapid reactivity. Subsequent in-depth characterization of the electronic structure of $[1]^+$ demonstrated that the complex exists as two essentially isoenergetic valence tautomers at 298 K, a triplet Cu^{II} -phenoxyl radical species, and a diamagnetic Cu^{III} species. Thus, the slower reactivity for $[1]^+$, in comparison to $[3]^+$ is presumably due to the presence of the Cu^{III} tautomer, which disfavours axial substrate binding in comparison to the Cu^{II} d^9 species. Substrate predisposition *via* substrate binding allows enzymes such as GO_{ase} to perform highly selective transformations under mild conditions. We were thus interested to investigate the electronic structure and reactivity of the one-electron oxidized asymmetric Cu salalen complex $[2]^+$, in comparison to $[1]^+$ and $[3]^+$. Metal complexes of the salalen ligand detailed herein have been investigated in catalysis, including the copolymerization of cyclohexene oxide with CO_2 (Cr),^[55] hydrosilylation (Mo),^[60] and asymmetric nitro-aldol chemistry (Cu).^[59] In this work we detail the electronic structure of $[2]^+$, and probe the reactivity of this interesting localized Cu^{II} -phenoxyl radical species.

2. Experimental

2.1 General Considerations

All solvents and reagents were obtained from commercial sources and used as received unless noted otherwise. The salalen ligand was prepared as reported previously.^[54] Data collection and structure solution for the crystal structures of **2** and $[2\text{H}]^+ \text{SbF}_6^-$ were conducted at the X-ray Crystallographic Laboratory, S146 Kolthoff Hall, Department of Chemistry, University of Minnesota. Details are available in the CIF files which have CCDC numbers 1563639 for **2** and 1563639 for $[2\text{H}]^+ \text{SbF}_6^-$. Cyclic voltammetry was performed using a BAS CV-40 potentiometer, a Ag wire reference electrode, a platinum disk working electrode, and a Pt wire counter electrode with 0.1M $^n\text{Bu}_4\text{NClO}_4$ solutions in CH_2Cl_2 . Ferrocene was used as an internal standard. X-band EPR spectra were collected with a Bruker EMX spectrometer using an ER041XG microwave bridge and an ER4102ST cavity. UV-Vis-NIR spectroscopy was performed using a Cary 500 dual-beam spectrophotometer. Variable temperature UV-Vis spectroscopy was performed using a Cary 50 spectrophotometer with a custom-designed immersable fiber-optic quartz probe with variable path length (1 and 10 mm; Hellma, Inc.). Constant temperatures were maintained either by a cooling bath (Kinetic Systems, New York) or a dry ice/acetone bath. Solution temperatures were directly monitored by insertion of an Omega temperature probe into the solutions. Variable temperature Evans method ^1H NMR measurements were performed on a Varian Inova 300 MHz instrument in CD_2Cl_2 , and diamagnetic corrections were estimated using Pascal's constants. Solvent contraction was accounted for in all variable temperature studies. Analytical services were provided by Desert Analytics (Tucson, AZ). Gas chromatography was performed on an HP5890 gas chromatograph equipped with a 30 m DB-1 column (J&WScientific, Inc.) and a flame ionization detector.

2.2 Synthesis

2.2.1 (N-(3,5-di-tert-butylsalicylidene)-N'-(2-hydroxide-3,5-di-tert-butylbenzyl))-trans-1,2-cyclohexanediamine Copper(II) (2)—(0.823 g, 1.5 mmol) of salalen ligand[54] was dissolved in CH_2Cl_2 (5 mL), and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.256 g, 1.5 mmol) was added as a solution in EtOH (6 mL). With stirring, NEt_3 (0.46 mL, 6.0 mmol) was added. The volume was reduced by half after 1 h and H_2O (2 mL) was added to precipitate a green solid. The solid was isolated and washed with EtOH and H_2O to afford **2** (0.809 g, 88 %). X-ray quality crystals were obtained by slow evaporation of a concentrated $\text{CH}_2\text{Cl}_2/\text{MeOH}$ solution. HRMS-ESI+ (m/z): $[\text{M}]^+$ calculated for $(\text{C}_{36}\text{H}_{54}\text{N}_2\text{O}_2\text{Cu})$, 609.3581; Found, 609.4041. UV-vis-NIR (λ_{max} [cm^{-1}] (ϵ [$\text{M}^{-1} \text{cm}^{-1}$]): 25,300 (6,250), 17,000 cm^{-1} (800). Anal. Calcd (found) for $\text{C}_{36}\text{H}_{54}\text{N}_2\text{O}_2\text{Cu} \cdot \text{H}_2\text{O}$: C, 68.81 (69.17); H, 8.98 (8.54); N, 4.46 (4.56).

2.2.2 (N-(3,5-di-tert-butylsalicylidene)-N'-(2-hydroxyl-3,5-di-tert-butylbenzyl))-trans-1,2-cyclohexanediamine Copper(II) hexafluoroantimonate ($[\text{2H}]^+\text{SbF}_6^-$)—**2** (0.222 g, 0.4 mmol) was dissolved in CH_2Cl_2 (5 mL) and solid AgSbF_6 (0.125 g, 0.4 mmol) was added. A purple suspension formed immediately. After 1 h the mixture was filtered through celite and recrystallized by pentane diffusion into the bulk CH_2Cl_2 solution. UV-vis-NIR (λ_{max} [cm^{-1}] (ϵ [$\text{M}^{-1} \text{cm}^{-1}$]): 25,000 (6,500), 19,000 (1,700), 17,600 (2,190), 8,600 (1,212). Brown/green crystals suitable for X-ray crystallography were isolated after one week. Anal. Calcd (found) for $\text{C}_{36}\text{H}_{55}\text{N}_2\text{O}_2\text{CuSbF}_6 \cdot 1.5 \text{CH}_2\text{Cl}_2$: C, 46.99 (47.32); H, 6.10 (5.78); N, 2.92 (2.99).

2.3 Resonance Raman Spectroscopy

Resonance Raman spectra were obtained on a SpectraPro-300i spectrometer (Acton Research) with a 2400-groove grating, a Beamlok 2060 Kr ion laser (Spectra-Physics), a holographic supernoch filter (Kaiser Optical Systems), and LN-1100PB CCD detector (Princeton Instruments) cooled with liquid N_2 . Spectra were collected on solvated samples (1 mM) in spinning cells (2 cm diameter, 1500 rpm) at 213 K, at an excitation wavelength $\lambda_{\text{ex}} = 413.1 \text{ nm}$ (20 mW), 90° scattering geometry, and 5 min data accumulation. Peak frequencies were calibrated relative to indene and CCl_4 standards (accurate to $\pm 1 \text{ cm}^{-1}$). During each Raman experiment, UV/Vis spectra were collected simultaneously on a PMA-11 CCD spectrophotometer (Hamamatsu) with a Potal MC-2530 (D_2/W_2) light source (Otsuka Electronic Co.).

2.4 X-ray Absorption Spectroscopy

Cu K-edge XAS data were collected at the Stanford Synchrotron Radiation Laboratory under dedicated ring conditions of 60–100 mA and 3 GeV. The data were recorded on the wiggler beam line 7-3. A Si (220) monochromator was used for energy selection and detuned (50%) to minimize higher harmonic components of the X-ray beam. The samples were formulated as frozen solutions in CH_2Cl_2 . The sample cell was pre-cooled in liquid N_2 before insertion into an Oxford Instruments CF1208 continuous flow liquid helium cryostat, in which the samples were maintained at 10–15 K during data collection. Data were measured in fluorescence mode with N_2 filled ionization chambers before and after the

sample. Internal energy calibration was performed by simultaneous measurement of the transmission signal through a Cu reference foil. The first inflection point of the copper reference data was aligned to 8980.3 eV. Data of four scans were averaged and were processed by fitting a smooth polynomial to the pre-edge region, which was background subtracted from the entire spectrum. A three region cubic spline was used to model the smooth background above the edge. Data were normalized by subtracting the spline and normalizing the postedge data to 1.0. EXAFS data were fit with the EXAFSPAK[68] program, using theoretical phase and amplitude parameters derived from FeFF 7.0.[69] Absorber-scatterer distances (R , Å) and Debye-Waller factors (σ^2 , Å²) were varied independently for each component in each fit. Additionally, the E_0 (eV) value, or the energy onset of photoionization, was also varied for each fit, but kept to a common value for all components of a given fit, and coordination numbers were kept constant. The intensities and energies of the $1s \rightarrow 3d$ pre-edge transitions for each complex were quantified by simultaneously fitting pseudo-Voigt line shapes to the data and the second derivative of the data using the EDG_FIT program. The energy position, half-width, and amplitude of each feature were allowed to vary within each fit. A background pseudo-Voigt function was used to model the rising absorption edge shape. The approximate peak area was measured as the product of the peak amplitude and the full width at half-maximum of the pre-edge feature. The stated peak areas are the average of the areas over the four energy ranges used, and standard deviations were calculated to estimate the variability of the fits.

2.5 Calculations

Geometry optimizations were performed using the Gaussian 09 program[70] (revision D. 01), the B3LYP[71, 72] functional, a polarized continuum model (PCM) for CH₂Cl₂ (dielectric $\epsilon = 8.94$),[73–76] and the 6–31G(d) basis set on all atoms as this double- ζ optimization has afforded good agreement with solid-state structural data of related salen systems.[20, 24, 25, 54, 77] The optimized geometries were confirmed as stationary states using frequency calculations. Single point calculations for energetic analysis were performed using the B3LYP functional and the TZVP basis set of Ahlrichs[78, 79] on all atoms with a PCM for CH₂Cl₂.

3. Discussion

3.1 Synthesis and Characterization of **2**

The Cu^{II} salen complex **2** (Figure 1) was synthesized in high yield by reacting the salen ligand[54] with CuCl₂•2H₂O and NEt₃ under aerobic conditions. The X-ray structure of **2** (Figure 2) with selected crystallographic data (Table 1) exhibits a slightly distorted square-planar geometry presumably due to the sterically demanding *ortho*-*t*Bu substituents, as well as the increased flexibility due to the partially-reduced salen ligand scaffold. This ligand asymmetry also results in a non-symmetric coordination sphere (Table 2): a slightly longer Cu–N bond is observed for the Cu–N_{aminophenoxide} (Cu–N(H) = 1.969 Å) in comparison to Cu–N_{iminophenoxide} (Cu–N(=) = 1.937 Å). This pattern is reversed for the Cu–O bond, where the Cu–O_{aminophenoxide} bond (1.874 Å) is shorter than Cu–O_{iminophenoxide} (1.893 Å). The distortion and non-symmetric coordination sphere observed for **2** is also observed for the reported Ni analogue.[54]

3.2 Electrochemistry

Redox processes for **2** were probed by cyclic voltammetry (CV) in CH₂Cl₂ using tetra-*n*-butyl ammonium perchlorate (ⁿBu₄NClO₄) as the supporting electrolyte. Complex **2** exhibits two quasi-reversible, one-electron redox processes at 0.15 V and 0.54 V vs. Fc⁺/Fc (Table 3) that are in line with the previously reported Ni derivative.[54] In general, the redox potentials for **2** are intermediate in comparison to the salen analogue **1**, and the fully reduced salan analogue **3** (Figure S1)[24, 52] in accord with the intermediate electron-donating ability of the salalen ligand in comparison to the salen and salan analogues. We have previously reported that [**1**]⁺ affords a Cu^{III} complex in the solid state, and that this electronic isomer is in equilibrium with a Cu^{II}-phenoxyl radical species in solution. This contrasts the temperature-invariant Cu^{II}-phenoxyl radical electronic structure for [**3**]⁺. [24] Thus, we were interested to isolate the one-electron oxidized [**2**]⁺, determine the electronic structure, and how the electronic structure would influence subsequent reactivity.

3.3 Chemical oxidation of **2** to [**2**]⁺

The chemical oxidation of **2** to afford [**2**]⁺ was probed under a number of different conditions. Employing the thianthrene radical oxidant (Th⁺•SbF₆⁻; 0.86 V vs. Fc⁺/Fc)[80] in CH₂Cl₂ solution cleanly afforded [**2**]⁺SbF₆⁻ as shown by UV-vis-NIR spectroscopy (Figure 3). The electronic absorption spectrum of **2** is typical of a d⁹, square-planar Cu complex, with a relatively intense charge transfer transition at 25,300 cm⁻¹ (ϵ = 6,250 M⁻¹ cm⁻¹) and a weaker d-d transition at 17,000 cm⁻¹ (ϵ = 800 M⁻¹ cm⁻¹, Figure 3).[24, 38, 77] Chemical oxidation by addition of Th⁺•SbF₆⁻ leads to the appearance of three new bands; a shoulder at *ca.* 19,000 cm⁻¹ (ϵ = 1,700 M⁻¹ cm⁻¹), and bands at 17,600 cm⁻¹ (ϵ = 2,190 M⁻¹ cm⁻¹) and 8,600 cm⁻¹ (ϵ = 1,212 M⁻¹ cm⁻¹). The broad shape and low intensity of the NIR band for [**2**]⁺ is suggestive of a localized ligand radical species,[21, 39, 54, 81, 82] however further confirmation of the electronic structure is detailed herein. Subsequent stability studies at 0.1 mM at 298 K revealed very little decomposition over a 15 h period (Figure 3 inset), however at higher concentrations [**2**]⁺ was observed to decompose in solution over time (*vide infra*).

3.4 Continuous Wave X-band Electron Paramagnetic Resonance (EPR)

The X-band EPR spectrum of a frozen solution of **2** collected at 77 K exhibits features consistent with a square-planar d⁹ Cu^{II} center (Figure 4), as observed for both **1** and **3**. [52] Oxidation of **2** to [**2**]⁺ results in the almost complete loss of an EPR signal, with < 4% of the original intensity by spin quantitation (Figure 4). Three possible electronic structures can account for the loss of EPR signal upon oxidation: 1) an antiferromagnetically-coupled Cu^{II}-phenoxyl radical species (*S* = 0); 2) a ferromagnetically-coupled Cu^{II}-phenoxyl radical species (*S* = 1) with a triplet energy difference outside of the range of X-band EPR; and 3) a Cu^{III} bis-phenoxide (*S* = 0). We employed additional experimental and theoretical analysis to further probe the electronic structure of [**2**]⁺.

3.5 Cu K-Edge X-ray Absorption Spectroscopy (XAS)

Cu K-edge XAS[83–85] was used to further probe the metal oxidation state and structure of **2** and [**2**]⁺ in frozen CH₂Cl₂ solution. The Cu K-edge data for **2** and [**2**]⁺ (Figure S2) are similar, with only a minor change in the 1s → 3d transition, or pre-edge, at 8979.5 eV for **2**,

and 8979.7 eV for $[2]^+$, indicating that the Cu^{II} oxidation state is maintained in $[2]^+$ upon one-electron oxidation. This is in contrast to the increase in the pre-edge of *ca.* 1 eV upon oxidation of **1** to $[1]^+$, which is indicative of metal-based oxidation (Cu^{II} to Cu^{III}).^[24] Extended X-ray absorption fine structure (EXAFS) for **2** and $[2]^+$ are well-fit to four N/O donors of the ligand, with a single shell distance of 1.92 Å for both complexes (Figure S3). The same average value for the N/O donors of **2** and $[2]^+$, presumably reflects the overall asymmetry in the structure, and the fact that EXAFS analysis typically cannot distinguish between first-shell atoms that differ in *Z* by 1 (*e.g.* O and N).^[86] The average value of 1.92 Å well-matches the average coordination sphere metrical data obtained by other methods (Table 2). Two additional parameters were required to fit the outer shell contributions to the EXAFS data: a shell of single scattering carbon atoms at 2.86 Å and 2.88 Å for **2** and $[2]^+$, respectively, and multiple scattering from these same carbon atoms at 3.12 Å and 3.13 Å for **2** and $[2]^+$, respectively (Table S1). Overall, the Cu K-edge XAS data supports a Cu^{II} -phenoxyl radical electronic description for $[2]^+$.

3.6 Resonance Raman (rR) Spectroscopy

Resonance Raman (rR) spectroscopy is an important tool for the characterization phenoxyl radical species.^[87] The rR spectra of **2** and $[2]^+$ (Figure 5) exhibit key differences upon oxidation, with vibrational modes associated with both phenoxyl $\pi \rightarrow \pi^*$ and phenolate $\rightarrow \text{Cu}^{\text{II}}$ LMCT transitions observable in the spectrum of $[2]^+$. The features at 1495 and 1597 cm^{-1} are assigned to characteristic phenoxyl radical C-O stretching (ν_{7a}), and $\text{C}_{\text{ortho}}\text{-C}_{\text{meta}}$ stretching (ν_{8a}) modes respectively.^[88–90] The phenolate bands at 1530 and 1627 cm^{-1} , are maintained upon oxidation to $[2]^+$, consistent with localization of the ligand radical on the Raman timescale.^[23, 91] Overall, the rR data supports the presence of both phenolate and phenoxyl ligands based on the observed vibrational modes, and thus localization of the ligand radical in $[2]^+$.

3.7 Variable-Temperature (VT) ^1H NMR and UV-Vis Spectroscopy

With confirmation of a localized Cu^{II} -phenoxyl radical structure for $[2]^+$, we further probed the electronic structure, and any possible temperature-dependence, using variable-temperature (VT) ^1H NMR and UV-Vis spectroscopies. Previous work has shown that $[1]^+$ exists in a reversible spin-equilibrium between a Cu^{II} -phenoxyl radical species ($S = 1$) and a high-valent Cu^{III} form ($S = 0$).^[24] The ^1H NMR spectrum of $[2]^+$ in CD_2Cl_2 at 293 K exhibits broad signals over a wide spectral range (Figure S4). Subsequent solution susceptibility measurements by the Evans method^[92] indicates a μ_{eff} of 2.67 BM (*ca.* 2 unpaired electrons at 293 K) consistent with a ferromagnetically-coupled Cu^{II} -phenoxyl radical species in solution. Cooling this solution to 193 K results in small decrease of the μ_{eff} to 2.36 (Figure 6), and this change is reversible upon warming to 293 K. We also probed the temperature-dependence of the UV-vis spectrum of $[2]^+$, and observe a small increase in the band at 17,500 cm^{-1} at low temperature (Figure 6). While this data is suggestive of a possible spin-equilibrium in solution, the data could not be reliably modelled over the available temperature range. The changes for $[2]^+$ are much smaller in comparison to the temperature-dependent susceptibility and UV-vis data reported for $[1]^+$ in solution.^[24] In

addition, DFT calculations predict the Cu^{III} electronic isomer for [2]⁺ to be much higher in energy (*vide infra*).

3.8 Theoretical Calculations on 2 and [2]⁺

Using the B3LYP[71, 72] functional with a polarized continuum model (PCM)[73–76] for CH₂Cl₂, a non-symmetric structure is predicted for the doublet **2** with coordination-sphere metrical parameters within ± 0.05 Å of the X-ray data (Table 2). Using the same DFT method, three different electronic configurations for [2]⁺ were considered: 1) a Cu^{III} complex ($S = 0$), 2) a Cu^{II} complex antiferromagnetically coupled to a phenoxyl radical (broken symmetry, $S = 0$), or 3) a Cu^{II} complex ferromagnetically coupled to a phenoxyl radical (triplet, $S = 1$). Consistent with the experimental XAS and rR data, the Cu^{II}-phenoxyl radical description is favored over the Cu^{III} solution by *ca.* 16 kcal mol⁻¹. The two Cu^{II}-phenoxyl radical electronic structures are nearly isoenergetic with the triplet favored by 0.3 kcal mol⁻¹. The significant magnetic susceptibility of [2]⁺ is consistent with a predominance of the triplet species in solution. The average coordination distance of the optimized $S = 1$ solution is within ± 0.02 Å of the experimental EXAFS data (Table 2). The phenoxyl radical is predicted to localize on the more electron-rich aminophenoxide moiety, with the associated magnetic orbitals shown in Figure 7. The phenoxyl radical (π) and Cu(II) d_{x²-y²} magnetic orbitals are orthogonal in accordance with the triplet spin state.[24, 93] This is consistent with the observation of both phenolate and phenoxyl bands in the rR spectrum of [2]⁺. Overall, both experimental and theoretical results support that [2]⁺ is a localized Cu^{II}-phenoxyl radical species.

3.9 Reactivity Studies

3.9.1 Decomposition of [2]⁺ in solution—In efforts to isolate X-ray quality crystals of [2]⁺, bulk oxidation of **2** at *ca.* 75 mM, using AgSbF₆ (0.65 V vs. Fc⁺/Fc) in CH₂Cl₂ at 298 K under an inert atmosphere. The resulting purple suspension was filtered and set aside to crystallize, and after one week green/brown crystals suitable for X-ray analysis were isolated. The X-ray structure is interpreted as a protonated phenoxide complex ([2H]⁺ SbF₆⁻) rather than a Cu^{II}-phenoxyl radical species ([2]⁺ SbF₆⁻) (Figure 8); the Cu-O and Cu-N bond lengths on the iminophenoxide side in [2H]⁺ contract considerably in comparison to **2**, while the protonated phenoxide (Cu-O(H)) lengthens (Figure 8). The DFT-optimized structure of [2H]⁺ has a Cu-O(H) bond length that matches within ± 0.002 Å of the X-ray metrical data. In addition, a H-bonding interaction between the protonated phenoxide and the SbF₆⁻ counterion is evident (O₁—F₃ = 2.727 Å). A frozen solution EPR spectrum of crystalline material exhibits typical features consistent with a square-planar d⁹ Cu^{II} center (Figure S5). Interestingly, a similar protonated species was recently crystallographically-characterized from a solution of a Cu(III) anilido complex.[94]

Intrigued by this result, a bulk oxidation performed under an inert atmosphere (*ca.* 50 mM) gave after one week a green/brown material. Subsequent purification using silica gel chromatography afforded a 2:1 ratio of **2** and Cu salen **1** in a total yield of 75 % based on the initial amount of **2**. We speculate that the recovered **2** was actually [2H]⁺, however, deprotonation readily occurs during purification (*vide infra*). Evolution of the Cu^{II} EPR signal for the decomposition of [2]⁺ over a 30 h period at a concentration of 3.3 mM (Figure

S6) provides additional insights into this transformation. The initial spectrum displays <2 % of the intensity in comparison to a concentration-matched sample of **2**, consistent with initial formation of $[2^{\bullet}]^+$. Over 30 h, a Cu^{II} signal appears, and reaches a maximum intensity of *ca.* 80 % relative to a concentration-matched sample of **2**. The frozen solution EPR spectrum of the isolated bulk oxidized material clearly shows a broadening of the parallel features, consistent with multiple Cu^{II} species in the sample (Figure S5). This EPR pattern can be fit to a 2:1 ratio of $[2\text{H}]^+$ (Figure S7), synthesized directly from equimolar amounts of triflic acid and **2**, and **1**, providing further confirmation for the stoichiometry of the decay process via purification of bulk material. While the decomposition of $[2^{\bullet}]^+$ was not probed further, we note that in order for the 2:1 ratio of $[2\text{H}]^+$ and **1** to form, an additional reducing equivalent is needed for electron balance. While the reducing agent was not identified, the *ca.* 75 % total yield from the bulk reaction points towards other Cu-ligated species that were not isolated.

3.9.2 Reactivity with Benzyl Alcohol—The stoichiometric reaction of $[2^{\bullet}]^+$ with the standard substrate benzyl alcohol was compared to the previously reported data for $[1]^+$ and $[3]^+$.^[52] While the first-order rate constant for $[1]^+$ varies linearly over the range [alcohol] = 0.05 – 1.0 M, providing a second-order rate constant of $k_2 = 1.3 \pm 0.1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 298 K, the reaction rate of $[3]^+$ saturates at high substrate concentration, and is well-fit by a k_{obs} expression including a substrate-binding pre-equilibrium (Figure 9). The parameters obtained for $[3]^+$ are $K = 3.0 \pm 0.2 \text{ M}^{-1}$ and $k_1 = 5.2 \pm 0.1 \times 10^{-3} \text{ s}^{-1}$, and the faster rate observed for $[3]^+$ vs $[1]^+$ is attributed to the substrate binding and preorganization that bears similarity to galactose oxidase. Reaction rate analysis for $[2]^+$ shows that the first-order rate constant varies linearly over the range [alcohol] = 0.05 – 1.0 M, similarly to $[1]^+$, providing a slightly faster second-order rate constant of $k_2 = 1.8 \pm 0.1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 298 K (Figure 9). The first-order decay of $[2^{\bullet}]^+$ in the presence of benzyl alcohol, monitored by UV-vis, directly correlates with the appearance of benzaldehyde as measured by GC analysis. Product yields are consistent with $[2^{\bullet}]^+$ reacting as a one-electron oxidant with the following reaction stoichiometry:

Overall, it appears that $[2^{\bullet}]^+$ reacts with benzyl alcohol in a similar manner to $[1]^+$, suggesting that even though the localized Cu^{II} -phenoxyl radical electronic structure matches that for $[3]^+$, the rigidity of the one imine arm limits the substrate binding step. In addition, the reaction profile for $[2^{\bullet}]^+$ is similar to that reported for the *para*-OMe substituted analogue of **4** (Figure 10), which also exhibits a localized Cu^{II} -phenoxyl radical electronic structure, and a rigid salen ligand framework.^[38] Interestingly, the reactivity of **5** (Figure 10) with ethanol and methanol proceeds via a substrate-binding mechanism, similarly to $[3]^+$.^[95] The rate constants are much slower in this case, reflecting the higher C-H bond strength of these substrates. An additional comparison of the benzyl alcohol single-turnover reactivity of $[1-3]^+$ with the Cu complexes of ligands **HL1** and **H₂L2** (the benzyl alcohol single-turnover reactivity of $[1-3]^+$ with the Cu complexes of ligands **HL1** and) can be made.^[96–99] The second order rate constant for the reaction of $[\text{Cu}^{\text{II}}(\text{L1}^*)(\text{NO}_3^-)]^+$ with benzyl

alcohol ($k_2 = 4.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) is similar to those determined for $[\mathbf{1-3}]^+$, while the comparative reaction rate for $[\text{Cu}^{\text{II}}(\text{HL}\mathbf{2}^*)(\text{OAc})]^+$ is 10-fold faster ($k_2 = 2.7 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$). The reasons for the rate acceleration for the latter system are unknown.[98] The 1:1 stoichiometry of the reaction of benzyl alcohol with $[\text{Cu}^{\text{II}}(\mathbf{L1}^*)(\text{NO}_3^-)]^+$ or $[\text{Cu}^{\text{II}}(\text{HL}\mathbf{2}^*)(\text{OAc})]^+$ reflects the accessibility of both phenoxyl and Cu^{II} oxidizing equivalents, while only the phenoxyl is accessible for $[\mathbf{1-3}]^+$. The square-planar geometry favoured by the salen-type ligands in $\mathbf{1-3}$ disfavours reduction to the Cu^{I} state.

4. Summary

In this work we have characterized the localized Cu^{II} -phenoxyl radical electronic structure of $[\mathbf{2}^*]^+$. On the basis of both experimental data and theoretical calculations, we show that the ligand radical is localized on the more electron-rich aminophenoxide. Unlike the oxidized Ni analogue,[54] $[\mathbf{2}^*]^+$ decomposes slowly in solution at RT, and a decay product $[\mathbf{2H}]^+$ is formed. Further analysis is consistent with the formation of $[\mathbf{2H}]^+$ and Cu salen $\mathbf{1}$ in a 2:1 ratio, however the mechanistic details have yet to be studied in detail. $[\mathbf{2}^*]^+$ is however stable at low concentrations (*ca.* 0.1 mM) at RT, and reactivity studies with benzyl alcohol show that this complex reacts similarly to $[\mathbf{1}]^+$, and does not exhibit a substrate-binding pre-equilibrium.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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1. We characterize a localized ligand radical via oxidation of an asymmetric Cu salan complex
2. The oxidized Cu salan complex decomposes over time to a protonated phenoxide and a Cu salen in a 2:1 ratio
3. Under single-turn-over conditions the oxidized Cu salan complex oxidizes benzyl alcohol without a substrate-binding pre-equilibrium

Figure 1.
Chemical structures of Cu salen (**1**), Cu salalen (**2**), and Cu salan (**3**) of relevance to this work.

Figure 2.

ORTEP plot of **2** (50% probability) using POV-Ray, including selected hydrogen atoms.

Selected average interatomic distances [$\text{\AA}$] and angles [$^\circ$]: Cu(1)-N(1): 1.969, Cu(1)-N(2): 1.937, Cu(1)-O(1): 1.874, Cu(1)-O(2): 1.893, C(1)-O(1): 1.329, C(20)-O(2): 1.305; Angles: N(1)-Cu(1)-N(2): 84.9, N(2)-Cu(1)-O(2): 92.9, O(1)-Cu(1)-O(2): 89.5, N(1)-Cu(1)-O(1): 92.9, N(1)-Cu(1)-O(2): 176.5, O(1)-Cu(1)-N(2): 175.7.

Figure 3.

Electronic spectra of 0.1 mM **2** (black) and $[\mathbf{2}]^+\text{SbF}_6^-$ (red) in CH_2Cl_2 at 298 K. $[\mathbf{2}]^+\text{SbF}_6^-$ was oxidized with $\text{Th}^+\text{SbF}_6^-$. Inset: Decay of 0.1 mM $[\mathbf{2}]^+\text{SbF}_6^-$ in CH_2Cl_2 at 298 K over 15 h.

Figure 4.

X-band EPR spectra for concentration-matched 2 mM samples of **2** (black) and simulation (red), in 2-MeTHF at 77 K, and $[2]^+$ (blue), in CH_2Cl_2 at 77 K. Simulation parameters: $g_{\parallel} = 2.217$, $g_{\perp} = 2.046$, $A_{\text{Cu}\parallel} = 193$, $A_{\text{Cu}\perp} = 31$, A values in cm^{-1} . Conditions: frequency = 9.3653 GHz; power = 2mW; modulation amplitude = 20 G.

Figure 5.
Resonance Raman (rR) spectra of (a) **2** and (b) [2[•]]⁺ at 213 K in CH₂Cl₂ (λ_{ex} = 413 nm).

Figure 6. Comparison of the VT solution susceptibility by ^1H NMR (black circles, CD_2Cl_2) and $17,500\text{ cm}^{-1}$ band intensity (red squares, CH_2Cl) for $[\mathbf{2}^\bullet]^+\text{SbF}_6^-$. See experimental section for details.

Figure 7.
Magnetic orbitals for the triplet ($S = 1$) electronic solution for $[2^*]^+$.

Figure 8.

ORTEP plot of $[2\mathbf{H}]^+\text{SbF}_6^-$ (50% probability) using POV-Ray, including selected hydrogen atoms. Selected average interatomic distances [$\text{\AA}$] and angles [$^\circ$]: Cu(1)-N(1): 1.947, Cu(1)-N(2): 1.910, Cu(1)-O(1): 2.022, Cu(1)-O(2): 1.846, C(1)-O(1): 1.379, C(20)-O(2): 1.334; Angles: N(1)-Cu(1)-N(2): 85.7, N(2)-Cu(1)-O(2): 95.7, O(1)-Cu(1)-O(2): 93.0, N(1)-Cu(1)-O(1): 87.9, N(1)-Cu(1)-O(2): 170.0, O(1)-Cu(1)-N(2): 164.5.

Figure 9.

Dependence of the pseudo-first-order rate constant k_{obs} on benzyl alcohol concentration for $[1]^+$ (circles, shown with linear fit), $[2]^+$ (triangles, shown with linear fit), and $[3]^+$ (squares, shown with saturation fit) at 298 K in CH_2Cl_2 . The concentration of $[2]^+$ was 0.1 mM in this study, thereby minimizing any decomposition over the time period of the experiment.

Figure 10.

Representative compounds that have been investigated for reactivity with benzyl alcohol under similar single-turnover reactivity conditions to $[1-3]^+$. Note one resonance form is shown for $[4]^+$ and $[5]^+$.

Table 1Selected Crystallographic Data for **2** and $[\mathbf{2H}]^+\text{SbF}_6^-$

	2	$[\mathbf{2H}]^+\text{SbF}_6^-$
Formula	$\text{C}_{36}\text{H}_{54}\text{N}_2\text{O}_2\text{Cu}$	$\text{C}_{36}\text{H}_{55}\text{N}_2\text{O}_2\text{CuSbF}_6$
Formula weight	610.36	847.14
space group	P 1	P 1
<i>a</i> (Å)	10.2792(9)	9.412(3)
<i>b</i> (Å)	13.6782(12)	16.187(5)
<i>c</i> (Å)	14.8362(19)	17.244(5)
α (°)	117.382(2)	111.733(4)
β (°)	97.513(2)	106.803(4)
γ (°)	103.518(2)	90.066(4)
<i>V</i> [Å ³]	1731.0(3)	2318.8(11)
<i>Z</i> , <i>D</i> _{calc} [g/cm ³]	2	1
<i>T</i> (K)	173	173
ρ_{calcd} (g cm ⁻³)	1.171	1.517
λ (Å)	0.71073	0.71073
μ (mm ⁻¹)	0.662	1.387
<i>R</i> indices ^a with <i>I</i> > 2σ(<i>I</i>) (data)	6793	16675
wR ₂	0.1110	0.1557
R ₁	0.0435	0.0575
Goodness-of-fits on F ²	1.011	1.071

^a Goodness-of-fit on F.

Table 2Coordination sphere metrical data for **2**, **[2]⁺**, and **[2H]⁺**.

Compound	Cu-O (Å)	Cu-O(=) ^a (Å)	Cu-N(=) ^a (Å)	Cu-N(H) (Å)
2				
X-ray ^b	1.874	1.893	1.937	1.969
XAS			1.92(1) ^c	
Calculated ^d	1.890	1.908	1.933	2.016
[2]⁺				
XAS			1.92(1) ^c	
Calculated (<i>S</i> = 1) ^d	1.955	1.868	1.909	2.008
[2H]⁺				
X-ray	2.022	1.846	1.910	1.947
Calculated ^d	2.024	1.856	1.896	1.891

^a (=) signifies imine portion of ligand.^b Average of two values from two molecules in the unit cell.^c Average Cu-O/Cu-N bond lengths from EXAFS fit.^d See Experimental Section for calculation details.

Table 3Redox Potentials of Cu^{II} complexes **1–3** Versus Fc⁺/Fc at 298 K.^a

Compound	$E_{1/2}^1$ (V)	$E_{1/2}^2$ (V)	Reference
1	0.45 (0.13)	0.65 (0.12)	[52]
2	0.15 (0.14)	0.54 (0.14)	This work
3	0.08 (0.14)	0.20 (0.13)	[52]

^aPeak-to-peak differences in brackets ($|E_{pa} - E_{pc}|$ in V).