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Ligand Effects on the Overpotential for Dioxygen Reduction by Tris(2-pyridylmethyl)amine Derivatives

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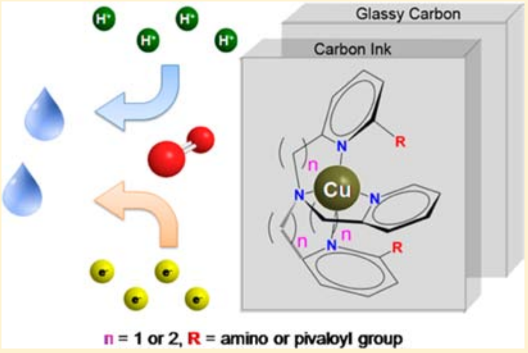
Ⓢ *Supporting Information*

ABSTRACT: A series of copper complexes based on the tris(2-pyridylmethyl)amine (TPA) ligand are examined for their oxygen reduction reaction (ORR) activity. Increasing the potential of the Cu$^{I/II}$ couple from 0.23 V vs RHE for $[Cu(TPA)(L)]^{2+}$ to 0.52 V for $[Cu(TEPA)(L)]^{2+}$ (tris(2-pyridylethyl)amine) at pH 7 or adding a hydrogen-bonding secondary coordination sphere does not increase the onset potential from 0.69 V vs RHE for the ORR. The underlying mechanism for the ORR is determined to be first-order in O_2 and second-order in Cu. The rate-determining step is found to not be Cu^{II} to Cu^{I} reduction, as seen in other systems. The rate-determining step is also not the protonation of an intermediate, but may be the reduction of a hydroperoxo intermediate. Pyrolysis of the Cu complex of TPA affords an inactive material; activity is recovered through addition of intact TPA to the electrode surface.



1. INTRODUCTION

Copper complexes are well-known to react with dioxygen, although relatively few studies examine their ability to catalyze the reduction of dioxygen to water.[1−5] This 4e$^-$ reduction is critically relevant to virtually all fuel cells, but empirical approaches have failed to deliver catalysts competitive with Pt-based systems. A rational approach involves modeling the active site of a multicopper oxidase, such as laccase, an enzyme that efficiently reduces O_2 to H_2O at a tricopper center.[6−8]

Copper complexes of phenanthroline and hexaazamacrocycles are active catalysts for the oxygen reduction reaction (ORR), but exhibit high overpotentials on the order of 600−700 mV.[9−12] We reported that a Cu complex of 3,5-diamino-1,2,4-triazole exhibits the lowest overpotential for the ORR for a nonbiological Cu complex, with an onset potential of 860 mV vs RHE at pH 13.[1,13] Recently, we also reported that salts of $[Cu(TPA)(L)]^{2+}$ (TPA = tris(2-pyridylmethyl)amine, L = water or solvent molecule) catalyze the ORR with an overpotential of 700 mV at pH 1, the lowest overpotential for a nonbiological Cu complex at this pH.[14]

The onset of the ORR in Cu complexes is influenced by a variety of effects. The primary coordination sphere has the principle influence on the reduction of dioxygen, with the lowest reduction potentials observed in complexes with nitrogen donors.[15] By tuning the sterics and electronics of the primary coordination sphere, $Cu_2{-}O_2$ complexes exhibiting O_2 in various binding modes have been isolated and characterized.[16−22] Ligand electronic effects are seen to mildly influence the Cu reduction potentials, though to a lesser extent than the sterics and geometry.[23−27] Apart from the primary coordination sphere, the secondary coordination sphere also heavily influences the performance of a catalyst, at least those involving hydrogen oxidation.[28,29]

Cu complexes of TPA have been widely studied for their reactivity toward dioxygen. For example, $[Cu(TPA)(MeCN)]^+$ reacts reversibly with dioxygen at −70 °C to give a μ-1,2-peroxo complex.[19] Since that initial report, many related derivatives have been prepared with differing stabilities of the Cu_2O_2 complex.[30−32] Substitution at the 6-position of the pyridines with amino groups stabilizes the peroxo complex.[33,34] With other substitutions, the initially formed superoxo complex can also be isolated.[22,35] Changing the methylene groups of TPA to ethylene raises the Cu$^{I/II}$ couple potential and changes the ligand coordination around the Cu(I) center from trigonal bipyramidal to square pyramidal for the Cu(I) complexes.[3,36] Copper complexes having higher reduction potentials, $[Cu(PMAP)(L)]^+$ (PMAP = 2-(pyridin-2-yl)-*N*-(2-(pyridin-2-yl)-ethyl)-*N*-(pyridin-2-ylmethyl)ethanamine) and $[Cu(TEPA)(L)]^+$ (TEPA = tris(2-(pyridin-2-yl)ethyl)amine), exhibit no reactivity toward dioxygen.[37]

Although exhibiting no reactivity toward O_2, $[Cu(TEPA)(L)]^+$ is of potential interest since its Cu$^{I/II}$ couple, being more positive than the $[Cu(TPA)(L)]^{+/2+}$ couple, may decrease the onset potential for the ORR (Chart 1). Similar substituent effects have been noted with methyl- and ethyl-substituted Cu−

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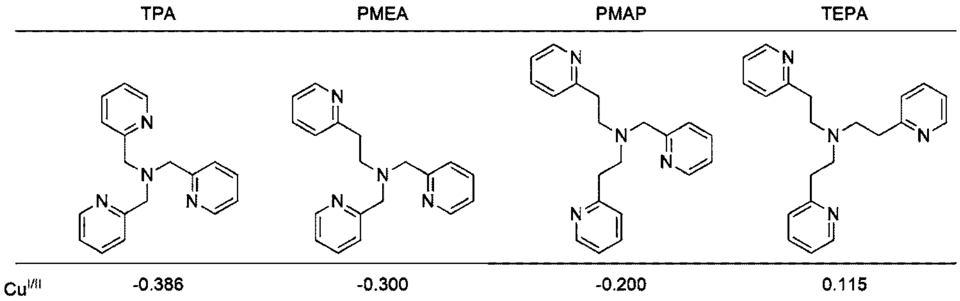
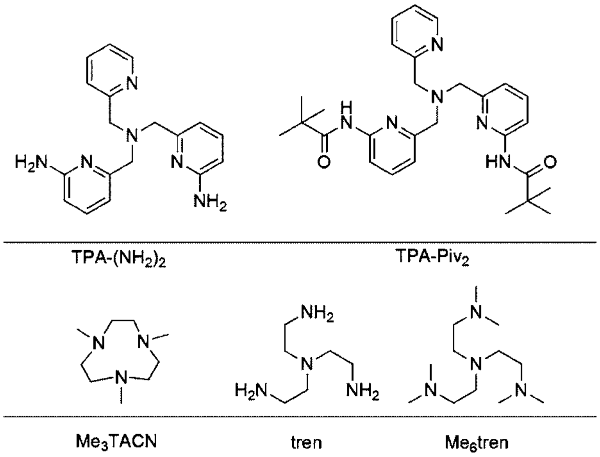
Chart 1. Diagrams of the Ligands TPA, PMEA, PMAP, and TEPA and the $E_{1/2}$ of the $Cu^{I/II}$ Couple in Acetone versus NHE[37]



phen complexes substituted at the 2- and 9-positions: the resulting Cu complexes display more positive reduction potentials by over 300 mV concomitant with a shift in the O_2 reduction onset potential by a similar quantity.[12]

In addition to changing the potential of the $Cu^{I/II}$ couple, TPA derivatives with specific functional groups could influence the ORR through the second coordination sphere. For example, substituents that can participate in hydrogen bonding can decrease overpotentials of reactions that require protons, as well as stabilize various dioxygen complexes.[28,38−40] The hydrogen-bonding groups provide a pathway to shuttle protons in and out of the metal centers required for efficient proton-coupled electron transfer (PCET). To evaluate this effect, we examined $[Cu(TPA\text{-}Piv_2)(L)]^{2+}$ (*N*,*N*′-(6,6′-(((2-pyridin-2-yl)-ethyl)azanediyl)bis(ethan-2,1-diyl))bis(pyridin-6,2-diyl))bis-(2,2-dimethylpropanamide)) and $[Cu(TPA\text{-}(NH_2)_2)(L)]^{2+}$ (6-(2-((2-(6-aminopyridin-2-yl)ethyl)(2-(pyridin-2-yl)ethyl)-amino)ethyl)pyridin-2-yl-amine), shown in Chart 2.[41−43]

Chart 2. Diagrams of Other Ligands Used in This Study



In addition to TPA-based ligands, chelating alkylamines, such as TACN[44,45] (1,4,7-triazonane) and tren[37,46−48] (tris(2-aminoethyl)amine), also give Cu complexes exhibiting dioxygen reactivity comparable to that of TPA derivatives. The dioxygen complex of $[Cu(^iPr_3TACN)(L)]^+$ reversibly interconverts between the side-on peroxo and the bis-*μ*-oxo species.[49] The Cu(I) derivative of Me_6tren (N^1,N^1-bis(2-(dimethylamino)ethyl)-N^2,N^2-dimethylethane-1,2-diamine) also reacts with O_2 to form a *trans*-*μ*-peroxo species.[46]

The above shows that the chemistry between Cu complexes and O_2 is well-established. However, there is no understanding as to whether any of these complexes exhibit ORR activity when immobilized at an electrode. More generally, the necessity of both ligand and metal for ORR reactivity in these systems is also unknown. In this paper, we examine Cu complexes with TPA, PMEA, PMAP, TEPA, TPA-Piv_2, TPA-$(NH_2)_2$, tren, Me_6tren, and Me_3TACN to evaluate parameters affecting the overpotential of the ORR and their metal and ligand dependencies.

2. EXPERIMENTAL SECTION

2.1. Physical Measurements. Elemental analyses were performed by the microanalysis laboratory located at the University of Illinois at Urbana−Champaign. TGA measurements were recorded with a CAHN THERMAX 500 thermogravimetric analyzer (Thermo Fisher).

2.2. Ligand Synthesis. Ligands TPA (tris(2-pyridylmethyl)-amine),[50] PMEA (2-(pyridin-2-yl)-*N*,*N*-bis(pyridin-2-ylmethyl)-ethanamine),[37] PMAP (2-(pyridin-2-yl)-*N*-(2-(pyridine-2-yl)ethyl)-*N*-(pyridine-2-ylmethyl)ethanamine),[37] TEPA (tris(2-(pyridin-2-yl)-ethyl)amine),[37] TPA-Piv_2 (*N*,*N*′-(6,6′-(((2-pyridin-2-yl)ethyl)-azanediyl)bis(ethan-2,1-diyl))bis(pyridin-6,2-diyl))bis(2,2-dimethyl-propanamide)), and TPA-$(NH_2)_2$ (6-(2-((2-(6-aminopyridin-2-yl)-ethyl)(2-(pyridin-2-yl)ethyl)amino)ethyl)pyridin-2-yl-amine)[42,43] were synthesized as previously reported. ^1H NMR spectra of the ligands matched the literature values. tren (tris(2-aminoethyl)amine) was purchased from Sigma-Aldrich and purified by distillation. Me_3TACN (1,4,7-trimethyl-1,4,7-triazonane) and Me_6tren (N^1,N^1-bis(2-(dimethylamino)ethyl)-N^2,N^2-dimethylethane-1,2-diamine) were purchased from Sigma-Aldrich and used without further purification.

Caution! *Perchlorate salts of metal ion complexes are potentially explosive. Only small amounts of materials should be prepared.*

2.3. Ink Preparation. Inks of the Cu complexes were prepared from complexes generated in situ. A solution of the ligands (9.1×10^{-5} mol) in 15 mL of ethanol was treated with $Cu(ClO_4)_2{\cdot}6H_2O$ (0.036 g, 9.1×10^{-5} mol, 99.999%, Alfa Aesar). After allowing the solution to stand for 15 min, Vulcan XC-72 carbon black (0.054 g, Cabot Corp.) and a solution of Nafion (60 *μ*L, 5 wt % in alcohols, Sigma-Aldrich) were added, and the suspension was sonicated for 30 min to disperse the carbon. The resulting ink (10 *μ*L) was then deposited on a glassy carbon electrode, which was dried under a stream of Ar.

2.4. Pyrolysis and Reconstitution Studies. *$[Cu(TPA)(L)](BPh_4)_2$ Supported on Vulcan XC-72 (1).* $CuSO_4{\cdot}5H_2O$ (0.017 g, 6.88×10^{-5} mol, 99.0%, Fisher Scientific) was dissolved in 1 mL of Milli-Q water. Vulcan XC-72 carbon black (0.080 g) was added, and the mixture was stirred for 5 min. TPA (0.020 g, 6.88×10^{-5} mol) was dissolved in 2 mL of Milli-Q water, and the resulting solution was added dropwise to the Cu/C mixture. After stirring the solution for 3 h at room temperature, $NaBPh_4$ (0.047 g, 1.38×10^{-5} mol, analytical reagent, Mallinckrodt) was added to the mixture. The resulting mixture was stirred overnight at room temperature. After centrifuging at 3000 rpm for 5 min, the liquid phase was discarded. The product was dried in vacuo at 90 °C for 3 h and used without further purification.

Pyrolyzed $[Cu(TPA)(L)](BPh_4)_2$ Supported on Vulcan XC-72 (2). $[Cu(TPA)(L)](BPh_4)_2$ supported on Vulcan XC-72 (0.042 g) was placed in a combustion boat (high-alumina, 5 mL capacity, Sigma-Aldrich). Pyrolysis was carried out at 800 °C under Ar for 6 h, and the product was used without further purification.

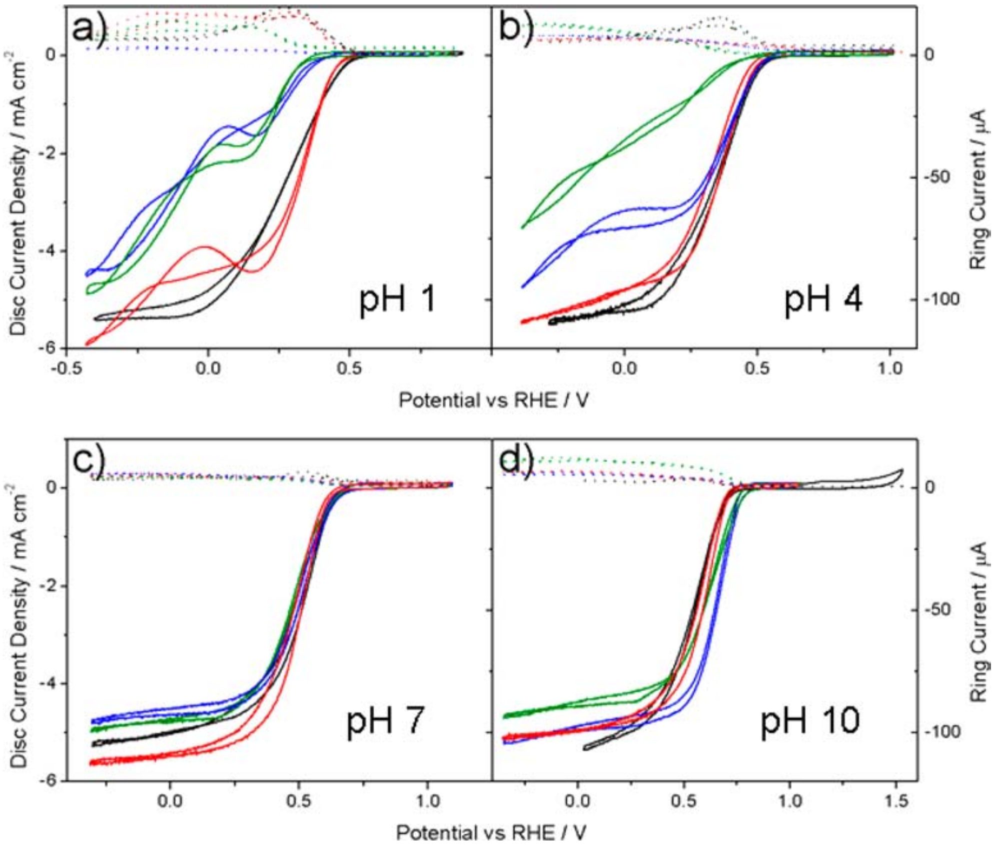


Figure 1. RRDE voltammograms of $[Cu(TPA)(L)]^{2+}$ (black), $[Cu(PMEA)(L)]^{2+}$ (red), $[Cu(PMAP)(L)]^{2+}$ (blue), and $[Cu(TEPA)(L)]^{2+}$ (green) at pH 1 (a), pH 4 (b), pH 7 (c), and pH 10 (d) under 1 atm of O_2 at 1600 rpm. Ring currents are plotted in dotted lines.

*Pyrolyzed [Cu(TPA)(L)](BPh$_4$)$_2$ Supported on Vulcan XC-72 Reconstituted with TPA (**3**).* Pyrolyzed $[Cu(TPA)(L)](BPh_4)_2$ supported on Vulcan XC-72 (0.007 g) was stirred in 5 mL of Milli-Q water for 5 min. To this solution was added TPA (0.001 g, 3.9×10^{-6} mol), and the resulting mixture was stirred for 3 h at room temperature. After centrifuging at 3000 rpm for 5 min, the liquid phase was discarded. The product was dried in vacuo at 90 °C for 3 h and used without further purification. Inks of **1**, **2**, and **3** were prepared using the procedure described above.

2.5. Electrochemical Experiments. Rotating ring-disk electrode electrochemistry (RRDE) was conducted with a CH Instruments 760C bipotentiostat and a Pine Instruments MSRX rotator. Experiments were performed in a two-compartment cell with an aqueous "no leak" Ag/AgCl (3 M KCl, ESA, Inc.) reference electrode separated from the working electrode by a Luggin capillary. A Pt mesh counter electrode was separated from the working electrode by a glass frit. The working electrode was a glassy carbon disk ($A = 0.196$ cm^2) with a Pt ring ($A = 0.093$ cm^2, Pine Instruments), which was cleaned by polishing with 0.5 μm diamond polish when needed. The Pt ring was held at 1.2 V vs RHE for all experiments, and the collection efficiency was determined to be 0.04 by comparison of the disk to ring currents for the 2e$^-$ reduction of O_2 to H_2O_2 for unmodified Vulcan XC-72. All experiments were calibrated to the reversible hydrogen electrode by flushing the cell with 1 atm of H_2 and monitoring the open-circuit potential after experiments were performed. All of the voltammetry was performed at a scan rate of 10 mV s^{-1} and at approximately 25 °C.

Solutions were made using Milli-Q purified water. RRDE experiments at pH 1 were performed in 0.1 M $HClO_4$ (70 wt % Optima grade $HClO_4$, Fisher Scientific). RRDE experiments at pHs 2−10 were performed in Britton-Robinson buffer consisting of 0.04 M H_3BO_3 (99.999%, Sigma-Aldrich), 0.04 M CH_3COOH (99.99%, Sigma-Aldrich), 0.04 M H_3PO_4 (85 wt % in H_2O, 99.99%, Sigma-Aldrich), and 0.1 M $NaClO_4$ (99.9%, Sigma-Aldrich). The pH was adjusted using 10 N NaOH (Analytical titration grade, Fisher Scientific). Solutions for pH 13 experiments were made by diluting 10 N NaOH with Milli-Q water. RRDE experiments for the pyrolysis and reconstitution studies were performed in pH 6 phosphate buffer (Fisher Scientific).

Mass flow rates were monitored with an FMA-78P4 controller and FMA-867A-V mass flow meters (Omega). The cell was an open flow cell, and all solutions were sparged with the gases for 400 s before any measurements were undertaken.

3. RESULTS

3.1. Varying TPA Alkyl Chain Length.

RRDE voltammetry experiments for the Cu(II) complexes of TPA, PMEA, PMAP, and TEPA are shown in Figure 1. At pH 1 (Figure 1a), $[Cu(TPA)(L)]^{2+}$ and $[Cu(PMEA)(L)]^{2+}$ display similar onset potentials of 0.53 V, but have different limiting behaviors. $[Cu(TPA)(L)]^{2+}$ exhibits diffusion-limited behavior, whereas $[Cu(PMEA)(L)]^{2+}$ has two different regions of limiting current. At potentials between 0.25 and −0.2 V, the RDE exhibits a sinusoidal profile. This profile is found at the same potential where considerable peroxide is detected at the ring. We speculate that the sinusoidal behavior is related to peroxide association with the $[Cu(PMEA)(L)]^{2+}$ complex since the sinusoidal behavior is not present on the return sweep. At more negative potentials, the ORR current increases monotonically and does not show limiting behavior. Reduction of O_2 by $[Cu(PMAP)(L)]^{2+}$ and $[Cu(TEPA)(L)]^{2+}$ both start at 0.38 V and similarly display two regions of reduction current.

At pH 4 (Figure 1b), $[Cu(TEPA)(L)]^{2+}$ still exhibits low activity, with an onset potential of 0.48 V and currents with no diffusion limits. $[Cu(PMAP)(L)]^{2+}$ exhibits an onset of ORR similar to that of $[Cu(TPA)(L)]^{2+}$ and $[Cu(PMEA)(L)]^{2+}$ at

Table 1. Number of Electrons Transferred for the ORR for $[Cu(TPA)(L)]^{2+}$, $[Cu(PMEA)(L)]^{2+}$, $[Cu(PMAP)(L)]^{2+}$, and $[Cu(TEPA)(L)]^{2+}$ and the $E_{1/2}$ for the $Cu^{I/II}$ Couple at pH 7 vs RHE[a]

	n at pH 1 (−0.15 V)	n at pH 4 (0.0 V)	n at pH 7 (0.15 V)	n at pH 10 (0.30 V)	$E_{1/2}$ $Cu^{I/II}$ (pH 7)
$[Cu(TPA)(L)]^{2+}$	4.0	3.6	3.8	4.2	0.23
$[Cu(PMEA)(L)]^{2+}$	3.2	3.6	4.0	4.0	0.37
$[Cu(PMAP)(L)]^{2+}$	2.3	2.5	3.6	3.4	0.42
$[Cu(TEPA)(L)]^{2+}$	2.2	1.6	3.7	3.7	0.52

[a] Potentials listed in the column headings are the potentials where the number of electrons transferred was determined.

0.57 V, but with a lower diffusion limited current. $[Cu(TPA)(L)]^{2+}$ and $[Cu(PMEA)(L)]^{2+}$ show very similar reactivity. Table 1 reports the number of electrons transferred as a function of pH, determined from the Koutecky−Levich equation using a standard method.[13,51] While the $[Cu(TPA)(L)]^{2+}$ complex exhibits a $4e^-$ reduction of O_2 to H_2O in the diffusion-limited region, complexes of the other three ligands show incomplete reduction, with both $[Cu(PMAP)(L)]^{2+}$ and $[Cu(TEPA)(L)]^{2+}$ exhibiting only $2e^-$ reduction.

Figure 1c shows that, once pH 7 is reached, all four complexes behave similarly, with onset potentials of 0.69 V and diffusion-limited currents. At pH 10 (Figure 1d), $[Cu(PMAP)(L)]^{2+}$ and $[Cu(TEPA)(L)]^{2+}$ have more positive onset potentials of 0.81 V than $[Cu(TPA)(L)]^{2+}$ and $[Cu(PMEA)(L)]^{2+}$ at 0.77 V. All four compounds show similar diffusion-limited currents. A plot of the onset potentials versus pH for the four compounds shows that, between pH 5 and 9, all four of these complexes exhibit the same onset (Figure 2). The number of electrons transferred at pH 7 is the same for all compounds, approaching the $4e^-$ expected for the complete reduction of O_2 to H_2O (Table 1). The potential of the $Cu^{I/II}$ couples for these complexes determined from cyclic voltammetry studies in pH 7 Britton−Robinson buffer are also found in Table 1.

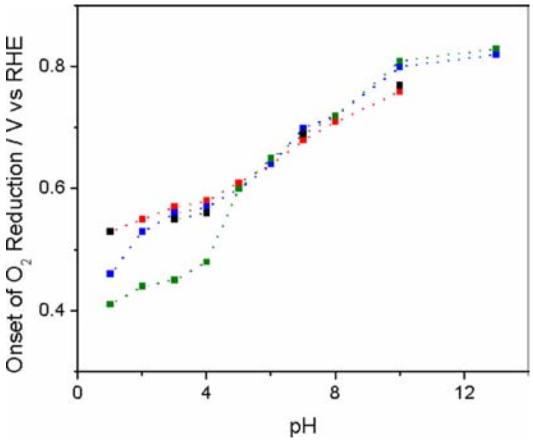


Figure 2. Plot of onset potential for O_2 reduction vs the solution pH for $[Cu(TPA)(L)]^{2+}$ (black), $[Cu(PMEA)(L)]^{2+}$ (red), $[Cu(PMAP)(L)]^{2+}$ (blue), and $[Cu(TEPA)(L)]^{2+}$ (green).

The influence of O_2 concentration on the ability of $[Cu(TPA)(L)]^{2+}$ to catalyze ORR was investigated. Decreasing the partial pressure of O_2 during the ORR by $[Cu(TPA)(L)]^{2+}$ by diluting it with Ar results in decreased limiting currents, as seen in Figure 3. The limiting current is linearly related to the partial pressure of O_2, displaying a first-order dependence on dioxygen in the overall reaction.

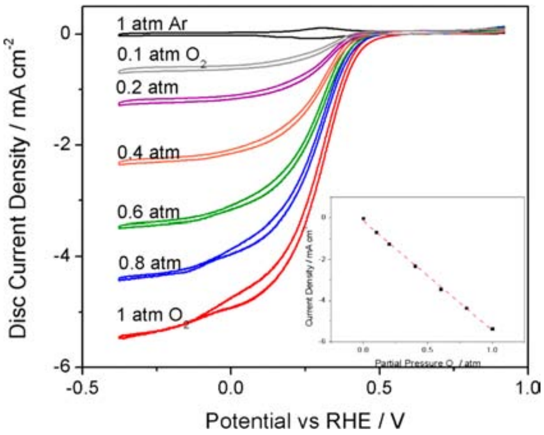


Figure 3. RRDE voltammograms of $[Cu(TPA)(L)](ClO_4)_2$ supported on Vulcan XC-72 in 0.1 M $HClO_4$ at 1600 rpm with different partial pressures of O_2 in an Ar atmosphere. Inset is a plot of the partial pressure of O_2 versus the limiting current.

3.2. Effect of Hydrogen-Bonding Substituents.

We investigated the compounds $[Cu(TPA-(NH_2)_2)(L)]^{2+}$ and $[Cu(TPA-Piv_2)(L)]^{2+}$ in order to probe the influence of hydrogen-bonding groups on the overpotential for the ORR. Under an atmosphere of Ar, these complexes supported on carbon exhibit reversible $Cu^{I/II}$ redox couples at 0.22 V for $[Cu(TPA-Piv_2)(L)]^{2+}$ and 0.42 V for $[Cu(TPA-(NH_2)_2)(L)]^{2+}$ (Supporting Information). The voltammetry exhibits multiple peaks, indicating the probable presence of Cu site heterogeneity due to different modes of association by the ligand with the C material. The introduction of dioxygen increases the cathodic current, as seen in Figure 4. The onset of the ORR for

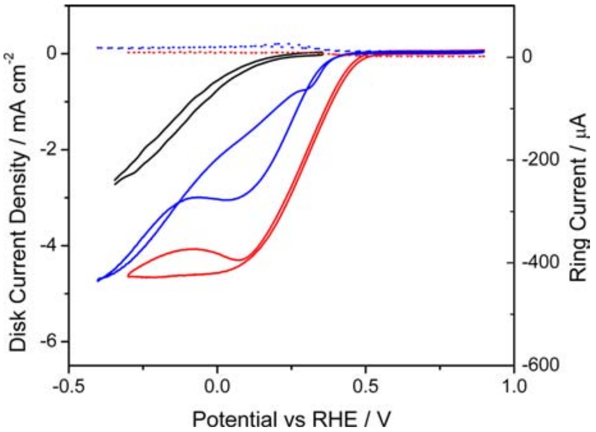


Figure 4. RRDE voltammograms of $[Cu(TPA-(NH_2)_2)(L)]^{2+}$ (red), $[Cu(TPA-Piv_2)(L)]^{2+}$ (blue), and Vulcan XC-72 (black) under 1 atm of O_2 at 1600 rpm in 0.1 M $HClO_4$. Ring currents are plotted in dotted lines.

$[Cu(TPA\text{-}(NH_2)_2)(L)]^{2+}$ occurs at 0.53 V, which is the same as that found for $[Cu(TPA)(L)]^{2+}$. $[Cu(TPA\text{-}Piv_2)(L)]^{2+}$ exhibits a more negative onset of 0.40 V, and a lower current density than $[Cu(TPA)(L)]^{2+}$. The lower current density observed for $[Cu(TPA\text{-}Piv_2)(L)]^{2+}$ is attributed to the $2e^-$ reduction of O_2 to H_2O_2. The dominance of the $2e^-$ pathway for the ORR by $[Cu(TPA\text{-}Piv_2)(L)]^{2+}$ is evidenced by the increased ring currents as well as the Koutecky−Levich plot (Supporting Information).

3.3. Alkylamine Derivatives. As discussed in the Introduction, Cu complexes of chelating alkylamines are known to react with dioxygen to give both the end-on and the side-on peroxo O_2 adducts. These complexes include $[Cu(tren)]^+$, $[Cu(Me_6tren)]^+$, and $[Cu(Me_3TACN)]^+$. We thus examined the ORR activity of these complexes. Figure 5 shows the ORR activity for $[Cu(tren)(L)]^{2+}$, $[Cu(Me_6tren)(L)]^{2+}$, and $[Cu(Me_3TACN)(L)]^{2+}$ at pH 1. Relative to $[Cu(TPA)(L)]^{2+}$ (0.53 V vs RHE), all three exhibit more negative onset potentials: 0.43 V vs RHE for $[Cu(tren)(L)]^{2+}$, 0.33 V for $[Cu(Me_6tren)(L)]^{2+}$, and 0.30 V for $[Cu(Me_3TACN)(L)]^{2+}$. Additionally, $[Cu(tren)(L)]^{2+}$ and $[Cu(Me_6tren)(L)]^{2+}$ only catalyze the $2e^-$ reduction of oxygen to hydrogen peroxide, as evidenced by the high ring currents and a Koutecky−Levich plot (Supporting Information). Voltammograms of the three alkylamine complexes under an Ar atmosphere do not exhibit the characteristic $Cu^{I/II}$ couple observed for the other complexes (Supporting Information).

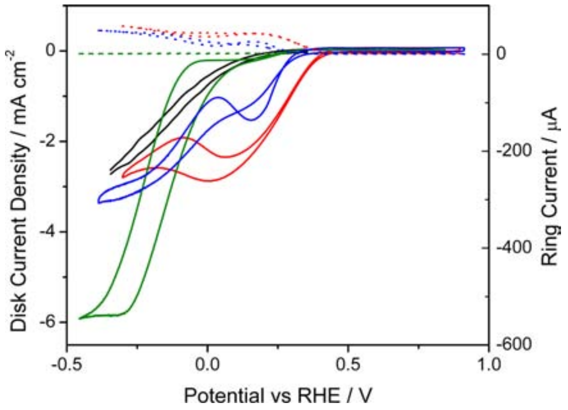


Figure 5. RRDE voltammograms of $[Cu(Me_3TACN)(L)]^{2+}$ (green), $[Cu(tren)(L)]^{2+}$ (red), $[Cu(Me_6tren)(L)]^{2+}$ (blue), and Vulcan XC-72 (black) under 1 atm of O_2 in 0.1 M $HClO_4$ at 1600 rpm. Ring currents are plotted in dotted lines.

3.4. Pyrolysis and Reconstitution. Some of the most effective nonprecious metal-containing ORR catalysts are produced by the pyrolysis of Fe-containing porphyrins and phthalocyanines. Indeed, these pyrolyzed systems are superior catalysts relative to the parent metallocycles.[52] We examined the pyrolysis of $[Cu(TPA)(L)]^{2+}$ to probe for similar beneficial effects. The expected Cu/TPA ratio is 1:1 in the complex, yielding a Cu/N ratio of 1:4. Elemental analysis revealed a 1:4.15 Cu/N ratio for $[Cu(TPA)(L)](BPh_4)_2$ supported on Vulcan XC-72. A 1:1.08 Cu/N ratio was recorded for pyrolyzed $[Cu(TPA)(L)](BPh_4)_2$ supported on Vulcan XC-72. As shown in Figure 6, pyrolysis of $[Cu(TPA)(L)](BPh_4)_2$ supported on Vulcan XC-72 resulted in a ca. 300 mV negative shift of the ORR onset potential, along with a decrease in current density at the diffusion-limited region. However, after reconstituting the pyrolyzed material with fresh TPA, the ORR onset potential and the current density reached at the diffusion limited region were comparable to those of unpyrolyzed $[Cu(TPA)(L)](BPh_4)_2$ supported on Vulcan XC-72.

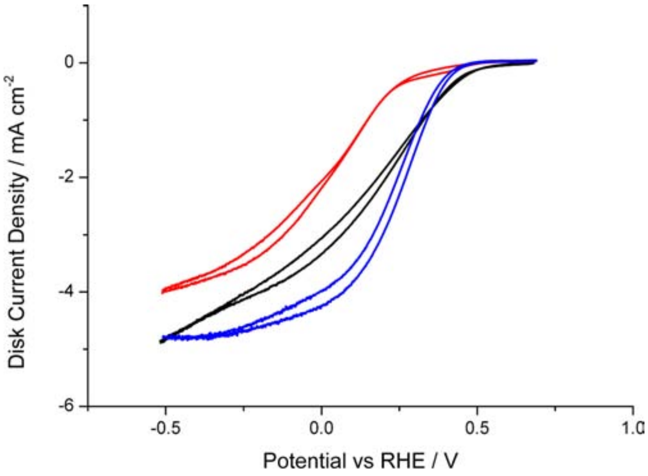


Figure 6. RRDE voltammograms of $[Cu(TPA)(L)](BPh_4)_2$ supported on Vulcan XC-72 (black), pyrolyzed $[Cu(TPA)(L)](BPh_4)_2$ supported on Vulcan XC-72 (red), and pyrolyzed $[Cu(TPA)(L)](BPh_4)_2$ supported on Vulcan XC-72 reconstituted with TPA (blue).

4. DISCUSSION

These results provide insight into the nature of the ORR active site in the $[Cu(TPA)(L)]^{2+}$ materials and point to features that could guide the design of catalysts with still greater ORR activity. By changing the methylene linkers of TPA to ethylene groups, the $Cu^{I/II}$ reduction potential of the complexes shifts to more positive potentials in both nonaqueous and aqueous solvents (Figure 1 and Chart 1). The onset of ORR, however, does not shift to more positive potentials as a result. The similarity in the onsets for ORR between $[Cu(TPA)(L)]^{2+}$, $[Cu(PMEA)(L)]^{2+}$, $[Cu(PMAP)(L)]^{2+}$, and $[Cu(TEPA)(L)]^{2+}$ at pH 7 likely indicates that the mechanism of the ORR for all four compounds is similar. Since the ORR onset does not shift with the $Cu^{I/II}$ potential in these complexes, it is likely that the rate-determining step in the ORR with these complexes is not the reduction of the cupric ions. Interestingly, the Cu(I) derivatives $[Cu(PMAP)]^+$ and $[Cu(TEPA)]^+$ exhibit no reactivity with O_2 in acetone, but they readily reduce O_2 under electrochemical conditions in water, as shown here.

The pH dependence of the onset of ORR for $[Cu(TPA)(L)]^{2+}$, $[Cu(PMEA)(L)]^{2+}$, $[Cu(PMAP)(L)]^{2+}$, and $[Cu(TEPA)(L)]^{2+}$ has three regions (Figure 2). At low pH, $[Cu(TPA)(L)]^{2+}$ and $[Cu(PMEA)(L)]^{2+}$ have a region with a slope of 5 mV/pH, whereas $[Cu(PMAP)(L)]^{2+}$ and $[Cu(TEPA)(L)]^{2+}$ have very negative onsets. The poor performance for the PMAP and TEPA complexes at low pH are likely due to easy protonation of the axial pyridyl ligand and deligation of the metal, as evidenced from the UV−vis spectra (Supporting Information). This pK_a is below pH 1 for $[Cu(TPA)(L)]^{2+}$ and $[Cu(PMEA)(L)]^{2+}$, between 1 and 2 for $[Cu(PMAP)(L)]^{2+}$, and between 4 and 5 for $[Cu(TEPA)(L)]^{2+}$. Above pH 4, all four complexes behave similarly with a slope of ~30 mV/pH. The 30 mV/pH is usually a sign of a $2e^-$ rate-determining step as it is half of the expected 60 mV/pH for a $1e^-$ step. The activity levels off at pHs above 10, likely due to Cu−OH formation and precipitation.

In an attempt to identify the rate-determining step (RDS) for the ORR by $[Cu(TPA)(L)]^{2+}$ and related complexes, a variety of modified ligands were tested. The H-bonding amino groups in $[Cu(TPA\text{-}(NH_2)_2)(L)]^{2+}$ affect neither the onset of the ORR nor significantly change the Tafel slope compared to $[Cu(TPA)(L)]^{2+}$ (Supporting Information). $[Cu(TPA\text{-}Piv_2)(L)]^{2+}$ has a more negative onset potential for ORR and a larger Tafel slope compared to $[Cu(TPA)(L)]^{2+}$, which is attributed to steric effects; that is, the pivalamide groups limit formation of Cu_2O_2 intermediates. While thermal stability of a coordinated peroxo species to a $[Cu(TPA)(L)]^{2+}$ complex is increased by the addition of amine and pivalamide groups, direct interaction between the amines and the coordinated peroxo has not been directly observed. Assuming that the amine-substituted pyridyl groups retain their coordination to the Cu center, the lack of change in the onset potential or Tafel slope when adding the amino groups implies that the RDS is likely not a protonation step.

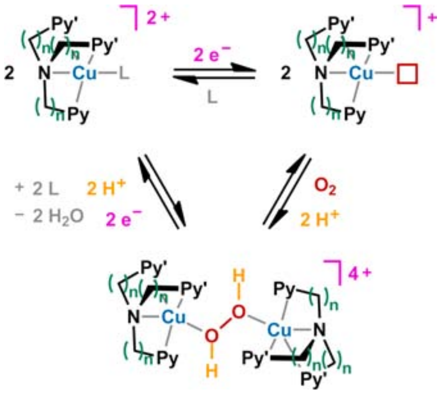
Using chelating alkylamines, such as tren, Me_6tren, and Me_3TACN, with Cu(II) results in more negative onset potentials compared to that observed for $[Cu(TPA)(L)]^{2+}$. Although all of the complexes used in this study have the same loading of 1 mol % on the Vulcan XC-72 support, only the alkylamine complexes do not exhibit a $Cu^{I/II}$ couple under an Ar atmosphere (Supporting Information). Vulcan XC-72 is a well-established support for molecular catalysts, and the ORR activity of unmodified Vulcan XC-72 at various pHs is characterized in various publications.[53,54]

Control experiments confirm that the ORR behavior of the supported alkylamine complexes is not due to the carbon support, since the onset for the ORR of Vulcan XC-72 is 0.20 V at pH 1, well below that of $[Cu(tren)(L)]^{2+}$ and $[Cu(Me_6tren)(L)]^{2+}$ (Supporting Information). Vulcan XC-72 is known to only catalyze the $2e^-$ reduction, yet $n = 4.3$ is found, which suggests that the ORR activity is due to $[Cu(Me_3TACN)(L)]^{2+}$ itself. There are two possibilities explaining the lack of an observable $Cu^{I/II}$ couple. First, electron transfer from the mostly graphitic carbon support to the aliphatic ligand might be poor and result in poor reduction or oxidation of the Cu center, which, in turn, leads to poor O_2 reactivity. An alternative explanation for the lack of a $Cu^{I/II}$ couple may be that the ligand must undergo a large reorganization upon reduction, resulting in small and largely separated reduction and oxidation peaks.

Determination of the RDS for ORR for $[Cu(TPA)(L)]^{2+}$ may lead to a better understanding of the ORR reaction catalyzed by Cu complexes. We determined in our previous paper that the RDS for the ORR catalyzed by this complex is likely a $2e^-$ reduction by invoking both the low Tafel slope (70 mV/dec) and the likely two copper center requirement from loading studies.[14] In this Article, we determined that the mechanism is first-order in O_2. We also determined that the RDS is not the reduction of Cu^{II} to Cu^{I}, nor is it a protonation event. The binding of O_2 to two Cu centers is also likely not the RDS, as it would give rise to a C-E type of mechanism, inconsistent with the observed Tafel slopes.[55,56] We suggest that the reduction of a bound H_2O_2 intermediate is a probable RDS (Scheme 1), as scission of the O−O bond is difficult. Indeed, peroxide reduction with $[Cu(TPA)(L)]^{2+}$ occurs at a somewhat more negative potential than that found for O_2 reduction in the same system.[14]

Results from pyrolysis and reconstitution studies demonstrate that intact copper complexes are required for catalysis. This result is in contrast to that found from catalysts prepared by pyrolysis of Fe- or Co-porphyrin or phthalocyanine, where the pyrolysis product exhibits more activity.[1,57] In the absence of any carbon support, TPA completely decomposes at 400 °C under Ar (Supporting Information). Although Cu is retained on the carbon after pyrolysis, the pyrolyzed material exhibits poor reactivity toward oxygen reduction. Interestingly, the reactivity can be reconstituted by the reintroduction of the ligand. This finding shows that Cu is available on the carbon following pyrolysis and not agglomerated to a degree that precludes association with the TPA ligand. Furthermore, Cu is neither present as an oxide nor bound up by other strongly donating ligands. Thus, the ligand plays a crucial role in defining the Cu active site. Further, Cu must exist as a molecular catalyst adsorbed on a carbon support in order to exhibit enhanced ORR activity.

Scheme 1. Proposed ORR Process of Cu Complexes with TPA Derivatives



5. CONCLUSIONS

Evaluating the influence of diverse ligands on the ORR by Cu complexes is a complex challenge. Changing the reduction potential of the Cu center does not seem to have a large effect on the overpotential for the ORR. Addition of hydrogen-bonding groups in the 6-position of TPA also does not lower the overpotential, while alkyl derivatives exhibit very large overpotentials. At pH 1, $[Cu(TPA)(L)]^{2+}$, $[Cu(PMEA)(L)]^{2+}$, and $[Cu(TPA\text{-}(NH_2)_2)(L)]^{2+}$ all have onsets for ORR within 30 mV of each other at pH 1, while exhibiting very different $Cu^{I/II}$ potentials. The reaction mechanism is found to be first-order in dioxygen. The rate-determining step for the ORR by $[Cu(TPA)(L)]^{2+}$ is then not the $Cu^{I/II}$ reduction, nor is it the protonation of a peroxo intermediate. Rather, O−O bond cleavage at the peroxide level is likely rate-determining. An intact $[Cu(TPA)(L)]^{2+}$ complex is required for the ORR reactivity seen here; pyrolysis leads to a less active catalyst with activity recovered by the addition of fresh ligand.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

RRDE voltammograms, Koutecky−Levich plots, Tafel plots, Randles−Sevcik plots, UV−vis spectra, and thermogravimetric analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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