



DOI:10.1002/ejic.201402687

A Copper Complex of a Noninnocent Iminophenol-Amidopyridine Hybrid Ligand: Synthesis, Characterization, and Aerobic Alcohol Oxidation

Zahra Alaji,^[a] Elham Safaei,^{*[a,b]} Linus Chiang,^[c] Ryan M. Clarke,^[c] Changhua Mu,^[c] and Tim Storr^{*[c]}

Keywords: Ligand design / Biomimetic synthesis / Copper / Homogeneous catalysis / Oxidation

Reaction of the noninnocent iminophenol-iminopyridine hybrid ligand HL^{IPIP}, where L^{IPIP} denotes [2-((*E*)-{(*E*)-2-[(*E*)pyridin-2-ylmethyleneamino]benzylidene}amino)-4,6-di*tert*-butylphenolate], with copper acetate afforded a copper complex, L^{APIP}Cu^{II}, in which one of the imine functional groups is oxidized to an amide during metal complexation. The new Cu^{II} complex is capable of catalyzing efficient aerobic alcohol oxidation under mild conditions. The crystal structure of L^{APIP}Cu^{II} exhibits a square-planar geometry with the Cu^{II} center coordinated by three nitrogen atoms and one oxygen atom. Electrochemical studies were conducted to evaluate the redox-active behavior of the complex, and the

Introduction

The chemistry of metal complexes with redox active ligands is of considerable interest in both bioinorganic and catalytic chemistry.^[1] Complexes of redox active ligands can be classified in two categories: (a) a metal-ligand radical $[M^{n+}(L^{-})]$, or (b) a high-valent metal $[M^{(n+1)+}(L^{-})]$ complex, depending on the relative energies of the redox-active orbitals.^[2] Oxidized metal complexes are known to exist in each form, and the factors that control the oxidation states of these complexes are currently under investigation.^[3] Given that these ligands possess various energetically accessible redox levels, tuning their redox processes can provide additional electron reservoirs for catalysis reactions. Much of this research is inspired by biological systems, in which ligand-radical species have been found to play key roles in a number of catalytic processes.^[4]

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201402687.

results showed a quasireversible reduction and a ligandbased oxidation process. The neutral species of $L^{APIP}Cu^{II}$ is EPR active, which is consistent with a paramagnetic electronic ground state (d⁹, S = 1/2), whereas the one-electron oxidized complex was X-band EPR silent. One-electron chemical oxidation of $L^{APIP}Cu^{II}$ gave a new species that can be attributed to a Cu^{II} -phenoxyl radical complex. Based on EPR measurements in conjunction with density functional theory calculations, $[L^{APIP}Cu^{II}]^+$ is proposed to have a triplet electronic ground state, exhibiting a weak ferromagnetic interaction between the Cu^{II} center and the coordinated phenoxyl radical.

Transition-metal complexes containing phenolate ligands have attracted significant attention as active site models of metalloenzymes, which include a transition-metal ion and a redox-active organic cofactor such as tyrosine.^[4c,5] Galactose oxidase (GAO) is the archetypical example, containing a copper(II)-tyrosyl (phenoxyl) radical as the key reactive intermediate for the two-electron oxidation of primary alcohols to aldehydes.^[6] Detailed structural, spectroscopic, and kinetic studies have demonstrated that the two-electron reaction catalyzed by GAO is performed by an active site that contains a single copper ion that shuttles through a one-electron process between Cu^I/Cu^{II} oxidation states, and, in addition, a copper-coordinated tyrosinate that is oxidized to a tyrosyl radical during the catalytic process (Scheme 1).^[7,8]

A great deal of effort has been invested in the design of biomimetic synthetic model systems of GAO incorporating redox active ligands for catalytic applications. The selective oxidation of alcohols in a facile and environmentally friendly manner is a desirable chemical transformation,^[1b] and, based on the GAO enzyme, copper complexes that include phenolate groups have led to the discovery of Cuphenolate/phenoxyl radical (or related) model systems that exhibit GAO-like alcohol oxidation activity.^[1f,6c,7,10] In the past decade, Wieghardt and Chaudhuri, Stack, as well as many other research groups, have published valuable reports of spectroscopic and functional models of GAO based on noninnocent Cu complexes of aminophenol li-

 [[]a] Institute for Advanced Studies in Basic Sciences (IASBS), 45137-66731, Zanjan, Iran E-mail: safaei@iasbs.ac.ir http://www.iasbs.ac.ir/chemistry/dep=3&ef=en&page=

personalpage.php&id=257 [b] Department of Chemistry, College of Sciences, Shiraz

University, 71454. Shiraz. Iran

[[]c] Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC V5A 1S6, Canada E-mail: tim_storr@sfu.ca

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Scheme 1. The active site and observable forms of GO.^[7,9]

gands.^[1a,3h,6c,9,11] These reports prompted us to undertake an investigation, described herein, of the synthesis and characterization of a new copper complex of an iminophenol-amidopyridine hybrid ligand and the associated catalytic activity towards aerobic alcohol oxidation under mild conditions (Scheme 2).



Scheme 2. The structure of $HL^{\rm IPIP}$ and the associated $Cu^{\rm II}$ complex $L^{\rm APIP}Cu^{\rm II}.$

Results and Discussion

Synthesis and Characterization of the Ligand $HL^{\rm IPIP}$ and Complex $L^{\rm APIP}Cu^{\rm II}$

The ligand HL^{IPIP} was synthesized through the sequential condensation of 2-aminobenzylamine with 3,5-DTBQ and then pyridine-2-carbaldehyde. Next, HL^{IPIP} was treated immediately with Cu(OAc)₂·2H₂O to afford the Cu complex L^{APIP}Cu^{II}. IR analysis of L^{APIP}Cu^{II} revealed a sharp band at 1642 cm⁻¹, attributed to the v_{C=O} stretch of an amide substituent, and this moiety was confirmed by X-ray analysis of the complex (see below). Oxidation of a coordinated imine group (coordinated imines are more susceptible to nucleophilic attack by H₂O or OH⁻) to a carboxamide, which can be started with nucleophilic attack by H₂O or OH⁻ on the imine, has been well-documented.^[12] This process can provide access to metal complexes that are difficult to synthesize. Although not studied further, Cu complexation likely facilitates the oxidation of the pyridine-imine of ligand HL^{IPIP} to form a pyridine-amide in $L^{APIP}Cu^{II}$.

X-ray Analysis

Red-brown crystals of the copper complex for X-ray analysis were obtained from an ethanol/dichloromethane (1:1) mixture. Crystal data for $L^{APIP}Cu^{II}$ is shown in Table 1 and selected bond lengths are listed in Table 2.

Table 1. Crystallographic data for LAPIPCuII.

	L ^{APIP} Cu ^{II}
Empirical formula	C ₂₇ H ₂₉ CuN ₃ O ₂
Formula weight	491.09
Crystal system	monoclinic
Space group	$P1 \ 2_1/c \ 1$
<i>a</i> [Å]	9.5598(5)
b [Å]	18.2903(9)
<i>c</i> [Å]	14.1699(8)
a [°]	90
β[°]	107.231(2)
γ[°]	90
$V[Å^3]$	2366.4(2)
Z	4
<i>T</i> [K]	150(2)
$\rho_{\text{calcd.}}$ [g/cm ³]	1.378
$\mu \text{ [mm^{-1}]}$	0.952
Reflections collected	57791
Significant reflections	9306
$\tilde{R[I} > 2.5\sigma(I)$	0.0450
$R_{\rm w} [I > 2.5\sigma(I)]$	0.0999
Goodness of fit	0.7317

The solid-state structure of $L^{APIP}Cu^{II}$ exhibits a distorted square-planar geometry (dihedral angle = 7.9°), with the Cu^{II} ion surrounded by three nitrogen atoms of amidate, pyridine, and an iminophenol (N2, N3, N4), with the final donor group of a phenolate oxygen atom (O5). (Figure 1).

The phenolate C(17)–O(5) bond length (1.322 Å) and the C–C bonds connected to the C(17)–O(5) moiety (1.422 Å

Table 2. Comparison of experimental and calculated (in parentheses) bond lengths (in Å) for the $L^{APIP}Cu^{II}$ and $[L^{APIP}Cu^{II}]^+$ complexes.

Bond	LAPIPCuII	[L ^{APIP} Cu ^{II}] ⁺	[L ^{APIP} Cu ^{II}] ⁺
		(S=1)	(S=0)
Cu(1)–N(2)	1.955 (1.958)	(1.976)	(1.974)
Cu(1) - N(3)	1.955 (1.972)	(1.976)	(1.978)
Cu(1) - N(4)	1.921 (1.924)	(1.951)	(1.953)
Cu(1) - O(5)	1.901 (1.895)	(2.005)	(2.006)
C(17)–O(5)	1.322 (1.326)	(1.273)	(1.272)
C(22)–N(4)	1.414 (1.412)	(1.392)	(1.391)
C(23)–N(4)	1.284 (1.297)	(1.305)	(1.305)
C(6)–N(2)	1.400 (1.400)	(1.385)	(1.385)



Figure 1. Molecular structure of $L^{APIP}Cu^{II}$. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are set at 50% probability.

and 1.412 Å) are also in good agreement with previously reported metal-phenolate structures.^[1f,11e,13] The Cu–O(5) (1.901 Å) bond length is consistent with the value reported for the Cu–O Tyr (Y272) in galactose oxidase $(1.9 Å)^{[14]}$ and some of its model complexes (1.904 Å).^[6e] The Cu–O (1.901 Å) and Cu–N (1.921, 1.955, 1.955 Å) bond lengths are slightly longer than those of the Cu^{II}-salen complex [Cu^{II}(Salen)] (Salen = diphenolate form of SalenH₂), *N*,*N'*bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexane-(1*R*,2*R*)diamine (Cu–O, 1.886 and 1.887 Å; Cu–N, 1.904 and 1.915 Å).^[15] The coordination geometry around the nitrogen donor, N(2), is planar, indicating that this nitrogen is three-coordinate (sp² hybridization) and is not protonated.^[16]

The ligand is thus in the di-anionic form when bound to Cu^{II} . ESI-MS analysis confirmed the presence of the L^{APIP} - Cu^{II} complex at m/z 491.2 (Figure S1). DFT calculations of $L^{APIP}Cu^{II}$ using the B3LYP functional are in good agreement with the solid-state data, with the predicted metrical parameters being within ± 0.02 Å of the experimental values (Table 2). The predicted spin density for $L^{APIP}Cu^{II}$ is shown in the Supporting Information (Figure S2) and is consistent with a $d_{x^2-y^2}$ ground state.

EPR Analysis of LAPIPCuII

A frozen toluene solution of the neutral species L^{APIP} -Cu^{II} is EPR active at 20 K (Figure 2), which is consistent with a paramagnetic electronic ground state (d⁹, S = 1/2). The Cu^{II} d⁹ paramagnetic ground state was also confirmed by the broadening of ¹H NMR peaks of $L^{APIP}Cu^{II}$ (Figure S3).



Figure 2. EPR spectrum of $L^{APIP}Cu^{II}$ (black) and simulation (red). Conditions: frequency: 9.3865 GHz; power: 2 mW; modulation frequency: 100 kHz; amplitude: 0.10 G; T = 20 K; concentration 1 mM in toluene.

The EPR simulation results shown in Table 3 indicate that the geometry of the neutral copper exhibits slight tetrahedral distortion, with rhombic symmetry.^[17] The pattern of g- and A-values also suggests a formal $d_{x^2-y^2}$ ground state for L^{APIP}Cu^{II}, as predicted by the calculations (see above).

Table 3. EPR parameters^[a] for L^{APIP}Cu^{II}.

	-						
	g_1	<i>g</i> ₂	<i>g</i> ₃	A ₁ ^[b] (Cu)	A ₂ ^[b] (Cu)	A ₃ ^[b] (Cu)	A _{1,2,3} ^[b] (N)
L ^{APIP} Cu ^{II}	2.025	2.046	2.170	29	29	217	14

[a] See experimental section for details, measured in toluene at 20 K. [b] Values in 10^{-4} cm⁻¹.

Electrochemistry

The redox processes of $L^{APIP}Cu^{II}$ were examined by cyclic voltammetry (CV) in CH_2Cl_2 . The Cu complex exhibits two quasireversible one-electron redox processes in the solvent window (Figure 3 and Table 4).

 $L^{APIP}Cu^{II}$ displays a quasireversible anodic redox process at 0.46 V, indicating a ligand-based oxidation to form a phenoxyl radical species (see below). The oxidation potential for $L^{APIP}Cu^{II}$ is comparable to the first oxidation potential reported for a large number of Cu^{II} -imino-phenolate complexes (ca. 0.45 V vs. Fc⁺/Fc in CH₂Cl₂), that exhibit ligand radical formation.^[3h,16a,18] The redox process at negative potentials (–1.61 V) could be a Cu^{II}/Cu^I reduction process, based on previously reported data.^[17a,19] However, we cannot rule out ligand reduction in this work.

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Figure 3. Cyclic voltammogram of $L^{APIP}Cu^{II}$. Conditions: 2.5 mm complex, 0.1 m NBu₄ClO₄, scan rate 100 mV/s, CH₂Cl₂, 298 K.

Table 4. Redox potentials of $L^{APIP}Cu^{II}$ vs. Fc⁺/Fc^[a] Peak to peak separation in parentheses.

	$E_{1/2}^{1}$ [V]	$E_{1/2}^2$ [V]
L ^{APIP} Cu ^{II}	-1.61 (0.21)	0.46 (0.19)

[a] Peak to peak difference for the Fc⁺/Fc couple at 298 K is 0.11 V.

Interestingly, the $L^{APIP}Cu^{II}$ redox process at negative potential is less reversible at 233 K than at 298 K (Figure S4); the changes could indicate considerable geometric rearrangement upon reduction from Cu^{II} to $Cu^{I,[19,20]}$

Electronic Spectroscopy Studies of $L^{APIP}Cu^{II}$ and $[L^{APIP}Cu^{II}]^+$

The electronic spectrum of $L^{APIP}Cu^{II}$ in CH_2Cl_2 is shown in Figure 4, and exhibits a series of bands in the visible region (Table 5). Oxidation titration experiments using the oxidant $[N(C_6H_4Br)_3]^+SbF_6^-$ from $0 \rightarrow 1$ equiv. at low temperature (198 K) revealed isosbestic points at 24500 and 19900 cm⁻¹, indicating clean conversion from L^{APIP} - Cu^{II} into $[L^{APIP}Cu^{II}]^+$. The intense band at 32000 cm⁻¹ is due to the oxidation by-product $N(C_6H_4Br_3)_3$. Upon oxidation to $[L^{APIP}Cu^{II}]^+$, a number of new bands appear in



Figure 4. Electronic spectra of 0.2 mM CH_2Cl_2 solutions of $L^{APIP}-Cu^{II}$ (black), $[L^{APIP}Cu^{II}]^+$ (red) and spectra during incremental oxidation (gray) with $[N(C_6H_4Br)_3]^+SbF_6^-$ at 198 K.

the visible region along with a broad low-energy band centered at 7400 cm⁻¹ ($3200 \text{ M}^{-1} \text{ cm}^{-1}$). The feature at 24000 cm⁻¹ (417 nm) is similar to that reported for other Cu-coordinated phenoxyl radical complexes,^[6e,21] and GAO.^[21,22] Whereas the oxidized form is stable in solution at low temperature, rapid decomposition occurs upon warming.

Table 5. Electronic absorption properties of the complex.^[a]

	$\tilde{v}_{max} \left(\epsilon_{max}, M^{-1} cm^{-1} \right)$
L ^{APIP} Cu ^{II}	31000 (9800, br), 29200 (7600, sh), 26700 (6300, sh), 25600 (8700), 24300 (9100), 20900 (6300)
[L ^{APIP} Cu ^{II}] ⁺	32000 (41400), 24000 (9700), 21500 (7600, sh), 20000 (5300, sh), 17300 (2000, sh), 7400 (2400, br)

[a] For details see the Experimental Section.

EPR Analysis of [LAPIPCuII]+

We investigated [L^{APIP}Cu^{II}]⁺ by variable-temperature EPR spectroscopy to better understand the electronic structure of this oxidized complex. The EPR spectrum of [LAPIP-Cu^{II}]⁺ and a concentration-matched sample of the neutral compound LAPIPCuII are shown in Figure 5. The lower spectral resolution of neutral LAPIPCuII in Figure 5 (measured in frozen CH₂Cl₂), compared with the spectra shown in Figure 2, is due to improved glassing ability of toluene. The EPR spectrum of [L^{APIP}Cu^{II}]⁺ exhibits a weak Cu^{II} signal with an intensity of approximately 0.35 in comparison to the concentration-matched neutral sample by spin quantitation. The weak axial Cu^{II} signal ($g_{\perp} = 2.03, g_{\parallel} =$ 2.20; $A_{\perp} = 35 \times 10^{-4} \text{ cm}^{-1}$, $A_{\parallel} = 186 \times 10^{-4} \text{ cm}^{-1}$) is likely due to decomposition of the oxidized complex upon transfer for EPR measurements. Variable-temperature EPR measurements of [L^{APIP}Cu^{II}]⁺ (Figure S5 and S6) show little change in the EPR spectrum from 110 to 20 K, suggesting that the oxidized form is either (i) a Cu^{III}-phenolato complex, (ii) a Cu^{II} complex antiferromagnetically coupled to



Figure 5. EPR spectrum of $L^{APIP}Cu^{II}$ (black), $[L^{APIP}Cu^{II}]^+$ (red), and simulated spectrum of oxidized decay product (blue). Conditions: frequency: 9.3783 GHz; power: 2 mW; modulation frequency: 100 kHz; amplitude: 6 G; T = 20 K; concentration: 0.3 mM in CH₂Cl₂.



phenoxyl radical (S = 0), or (iii) a Cu^{II} complex ferromagnetically coupled to a phenoxyl radical (S = 1) with large zero-field splitting.^[23] A large zero-field splitting can result in EPR transitions outside of the energy range of X-band EPR.^[24] We thus turned to theoretical calculations to gain further insight into the oxidized complex (see below).

Theoretical Calculations on [LAPIPCuII]+

DFT calculations of [L^{APIP}Cu^{II}]⁺ were performed by using the B3LYP functional/TZVP basis set combination and a polarized continuum model (PCM) for CH₂Cl₂ (dielectric $\varepsilon = 8.94$). This species can be described as one of the following: (i) a Cu^{III}-phenolato complex, (ii) a Cu^{II} complex antiferromagnetically coupled to phenoxyl radical (S = 0), or (iii) a Cu^{II} complex ferromagnetically coupled to a phenoxyl radical (S = 1). The calculations predict that the S =1 triplet solution ($\hat{S}^2 = 2.02$) is favored by 0.4 kcal/mol in comparison to the broken symmetry (BS, $\hat{S}^2 = 1.02$; Cu^{II} complex antiferromagnetically coupled to phenoxyl radical) electronic structure. The singlet solution is predicted to be approximately 11 kcal/mol higher in energy. The predicted spin densities for the triplet and BS solutions are shown in Figure 6, and they result in an exchange coupling J of 140 cm⁻¹, calculated by using the Yamaguchi equation [Equation (1)], which is applicable for systems from the strong to weak exchange limit.^[25,26]

$$J = \frac{E_{\rm HS} - E_{\rm BS}}{\langle \hat{S}^2 \rangle_{\rm HS} - \langle \hat{S}^2 \rangle_{\rm BS}} \tag{1}$$



Figure 6. Spin density plot of $[L^{APIP}Cu^{II}]^+$, triplet (left), and broken symmetry solution (right). See the Experimental Section for calculation details.

The calculations predict a lengthening of the Cu– O(phenoxyl) bond (1.895 to 2.005 Å) upon oxidation (Table 2), matching other reports for coordinated phenoxyl radicals.^[11e,13b,18,27] The increased Cu–O bond length can be attributed to the decline of the electron-donating ability of phenoxyl species relative to the phenolato moiety. In addition, the C–O bond is predicted to shorten upon oxidation from phenolate to phenoxyl (1.326 to 1.273 Å) (Table 2). This feature is consistent with a quinoid structure for the ring and thus a radical character for this moiety (Scheme 3).

Catalytic Activity of LAPIPCuII Complex

The synthesized copper complex L^{APIP}Cu^{II} was employed for the aerobic oxidation of a large number of structurally diverse alcohols to the corresponding aldehydes (Scheme 4).



Scheme 4. Catalysis conditions relevant to Table 8.

Our initial studies focused on determining the optimal conditions (base, solvent) for the conversion of a representative alcohol (benzyl alcohol) into the corresponding aldehyde (Table 6). We have found that the addition of base is essential for alcohol activation. Compared with previous reports,^[11g,29] intriguing features of this catalytic system include the efficient use of oxygen as the oxidant, high yield and high selectivity, the use of acetonitrile as a relatively green solvent,^[4c,30] and KOH as a low-cost base under mild conditions (room temperature) (Table 6, entries 5, 9, and 10). Control runs in the absence of catalyst at room temperature yielded no product. It is worth noting that KOH-mediated synthesis of imine from aerobic oxidation of alcohol has been reported to take place at high temperature using toluene as solvent.^[31]

Table 6. The effect of base and solvent on the aerobic oxidation of benzyl alcohol catalyzed by $L^{\rm APIP}Cu^{\rm II}$.

Entry	Base (equiv.)	Solvent	Time [h]	Conversion [%]
1	$Cs_2CO_3(2)$	toluene	6	70
2	$Cs_2CO_3(2)$	THF	6	95
3	$Cs_2CO_3(2)$	<i>n</i> -hexane	6	37
4	$Cs_2CO_3(2)$	MeCN	7	97
5	KOH (2)	MeCN	4	96
6	$NEt_3(2)$	MeCN	6	2
7	$Na_2CO_3(2)$	MeCN	24	2
8	$K_2CO_3(2)$	MeCN	24	38
9	KOH (3)	MeCN	3	98
10	KOH (1)	MeCN	5	100
11	KOH (0.5)	MeCN	5	93

A number of outstanding GO-inspired models have been developed for the aerobic oxidation of benzyl alcohol and these are summarized in Table 7. A mechanistically faithful, catalytic model of GO was first reported in 1998 by Stack et al.^[6f] The best results have been obtained by Wieghardt et al. with a very nice set of complexes in which the redox chemistry during the catalytic cycle is ligand-based.^[10d,28,32] As inferred from Table 7, our synthesized copper complex



Scheme 3. Canonical forms of phenoxyl radicals.^[7]



is a versatile catalytic system that catalyzes the oxidation of benzyl alcohol to bezaldehyde with a good turnover number of 260 after 6 h (Figure S7).

Table 7. Aerobic oxidation of benzyl alcohol catalyzed by galactose oxidase inspired model complexes.

Author	Year	Yield [%]	TON	Time [h]	Ref.
Stack et al.	1998	_	400	20	[6f]
Wieghardt et al.	1998	63	_	12	[10d]
Wieghardt et al.	1999	55	_	20	[28]
Thomas et al.	2002	_	220	48	[1a]
Wieghardt et al.	2004	_	95	10	[4c]
Chaudhuri et al.	2008	72	_	16	[11c]
Paine et al.	2012	_	62	7	[4h]
Safaei et al.	2014	_	260 ^[a]	6	this work

[a] TON reaction conditions: benzyl alcohol (2 M, 1 mL), KOH (1 M, 0.28 g), catalyst complex (2 mM, 0.005 g) in anhydrous CH₃CN (5 mL).

To help elucidate the mechanism, we conducted kinetic studies using the initial rate method and an experiment of anaerobic alcohol oxidation under turnover conditions with benzyl alcohol. The kinetics of the catalytic benzyl alcohol

Table 8. LAPIPCuII-catalyzed aerobic oxidation of alcohols.

oxidation reaction was measured by variation of total concentration of $L^{APIP}Cu$ and benzyl alcohol under 1 bar of oxygen in acetonitrile. From these data (Figures S8 and S9) the reaction was deduced to be first order in both Cu complex and substrate [Equation (2)].

$$Rate = k [complex][benzyl alcohol]$$
(2)

The observed first-order dependence of the rate on the complex and substrate indicate the composition of activated complex; in other words, one molecule of complex is utilized for the two-electron oxidation of one molecule of benzyl alcohol.^[11c] In a typical anaerobic experimental setup, to a mixture of benzyl alcohol (2 M, 1 mL) and KOH (1 M, 0.28 g) in anhydrous CH₃CN (5 mL) was added the complex (2 mM, 0.005 g) for 12 h. Under anaerobic conditions, the copper complex oxidizes benzyl alcohol to benzaldehyde stoichiometrically. Then the reaction was opened and stirred for 10 h under oxygen atmosphere (1 bar) to regenerate the active catalyst and lead to catalyzed oxidation of benzyl alcohol in relatively good yield (100 TON). Unfortunately, it was not possible for us to survey the kinetic isotope effect as examined in previous reports,^[4c, 6f, 32] how-



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ever, the lack of observed reactivity towards primary and secondary alkyl alcohols (Table 8, entries 15-17) at 298 K shows the limitation of this catalyst towards substrates with higher Ca-H bond strengths. Similar reactivity trends are found for GOase, which oxidizes primary alkyl alcohols at rates approximately 100 times slower than benzylic substrates.^[6f] On the basis of the kinetic studies and the anaerobic experiment, we can infer that the mechanism for the alcohol oxidation is similar to that proposed for the enzyme galactose oxidase (Scheme 1) and a number of reported functional model systems.^[1a,4c,7,28] Based on the optimized conditions determined from Table 6 we screened a variety of alcohol substrates as detailed in Table 8. A number of primary and secondary benzylic alcohols, including those with both electron-withdrawing and -donating groups, were selectively converted into the corresponding benzaldehydes in excellent yields under the optimal reaction conditions (>94%, Table 8, entries 1–13).

No overoxidation of the aldehyde to the carboxylic acid was observed by GC analysis. These results show that electronic effects do not seem to have a significant effect on the final product yields for electron-rich and electron-deficient benzylic substrates. An allylic alcohol could be effectively oxidized to afford excellent yield of the corresponding carbonyl product (Table 8, entry 14). However, this method was not applicable to the oxidation of primary and secondary aliphatic alcohols (Table 8, entries 15-17). In general, heteroatom-functionalized alcohols are regarded as highly challenging substrates for aerobic oxidation due to their strong coordination ability to transition-metal catalyst systems, and resulting deactivation. However, we found that our protocol was effective in the oxidation of 4-(methylthio)benzyl alcohol to afford the expected aldehyde, which further confirmed the superior capability of L^{APIP}Cu^{II} in oxidizing similar substrates (Table 8, entry 7).

Conclusions

A new copper complex of a noninnocent iminophenolpyridine hybrid ligand was synthesized and characterized. It is evident from X-ray crystallography analysis that L^{APIP}-Cu^{II} exists as a distorted square-planar Cu^{II} structure coordinated by pyridine, iminophenol, and amidate nitrogen atoms as well as one phenolate. Cyclic voltammetry measurements showed two quasireversible redox events for the Cu complex, suggesting both the formation of a phenoxyl radical species in the region of the anodic peak and a metalcentered redox (Cu^{II}/Cu^I) process at low potentials. Chemical one-electron oxidation of LAPIPCuII yielded a new species that can be assigned as a Cu^{II}-phenoxyl radical moiety analogous to the active Cu^{II}-tyrosyl radical form of galactose oxidase. EPR studies, in conjunction with theoretical analysis, point to a triplet ground-state for [L^{APIP}Cu^{II}]⁺, due to ferromagnetic coupling of the Cu^{II} (d⁹) metal center and phenoxyl radical. This copper complex is capable of efficient aerobic oxidation of alcohols under mild conditions.

Experimental Section

Materials and Methods: All chemicals were purchased from Merck and used as received. Solvents were purified before use by standard methods whenever necessary. Manipulations were performed under aerobic conditions. 3,5-Di-tert-butylcyclohexa-3,5-diene-1,2-dione (3,5-DTBQ) was synthesized according to a modification of a reported procedure.^[33] Electronic spectra were obtained with a Cary 5000 spectrophotometer with a custom-designed immersible fiberoptic quartz probe with variable path length (1 and 10 mm; Hellma, Inc.). IR spectra were recorded in the solid state with an FTIR Bruker Vector 22 spectrophotometer in the 400–4000 cm⁻¹ range. NMR spectra were recorded at 400 MHz with a Bruker DRX spectrometer in CDCl₃ solution. The chemical shifts were referred to TMS using the residual signals from the solvent. Cyclic voltammetry (CV) was performed with a PAR-263A potentiometer, equipped with a Ag wire reference electrode, a glassy carbon working electrode, and a Pt counter electrode with 0.1 M Bu₄NClO₄ solutions in CH₂Cl₂. Ferrocene was used as an internal standard. Mass spectra (positive ion) were obtained with an Agilent 6210 TOF ESI-MS instrument. The magnetic measurements were obtained by using Evan's method. NMR and EPR spectra were collected with a Bruker EMXplus spectrometer operating with a premiumX Xband (ca. 9.5 GHz) Microwave Bridge.

Low-temperature measurements of frozen solutions were recorded with a Bruker helium temperature-control system and a continuous flow cryostat. Samples for X-band measurements were placed in 4 mm outer-diameter sample tubes with sample volumes of approximately 300 μ L. EPR spectra were simulated with Easy Spin 3.1.7 software.^[34]

Ligand HL^{IPIP} and L^{APIP}Cu^{II}: L^{APIP}Cu^{II} complex was synthesized by the following template reaction. First, to a solution of 3,5-DTBQ (0.22 g, 1 mmol) in acetonitrile (4 mL) was added 2-aminobenzylamine (0.122 g, 1 mmol), and the reaction solution was stirred for 30 min at the room temperature in the presence of air. After some minutes, a yellow precipitate appeared, which was filtered and used in the next step. To a stirred suspension of the yellow precipitate (0.324 g, 1 mmol) in acetonitrile, was added pyridine-2-carbaldehyde (0.096 mL, 1 mmol). After 1 min of stirring, Cu(OAc)₂·2H₂O (0.199 g, 1 mmol) was added to the reaction mixture, then NEt₃ (2 equiv.) was also added. The red-brown solution was stirred at 298 K for 4 h to afford a red-brown precipitate of L^{APIP}Cu^{II}. The filtrate was left undisturbed to afford red-brown microcrystals (0.309 g, 63% yield) by evaporation from dichloromethane/acetonitrile solution. X-ray-quality dark-red single crystals were grown from a 1:1 solvent mixture of dichloromethane/ ethanol or *n*-hexane/dichloromethane. IR (KBr): $\tilde{v}_{max} = 2959$ (C-H), 1642 (C=O), 1466 (C=N), 802 (=C-H bending) cm⁻¹. ESI-MS: m/z (%) = 983.3 (40) [(L^{APIP}Cu^{II})₂]⁺, 491.2 (100) [L^{APIP}Cu^{II}]⁺ (Figure S1). C₂₇H₂₉CuN₃O₂·0.35C₆H₁₄: calcd. C 67.05, H 6.55, N 8.06; found C 66.79, H 6.61, N 7.76. Magnetic susceptibility: μ_{eff} = 1.56 μ_B (Evan's method).

Oxidation of L^{APIP}Cu^{II}: Under a nitrogen atmosphere at 195 K, an aliquot of a CH₂Cl₂ solution of L^{APIP}Cu^{II} (6.7 mm, 150 µL) was added to CH₂Cl₂ (3.0 mL). Monitored by UV/Vis/NIR, a solution of [N(C₆H₃Br₂)₃]SbF₆ in CH₂Cl₂ (9.9 mM) was added in 10 µL increments, resulting in conversion into [L^{APIP}Cu^{II}]⁺ after 75 µL of oxidant had been added.

Catalytic Activity of $L^{\rm APIP}Cu^{\rm II}$ Complex for Alcohol Oxidation

Alcohol oxidation experiments were carried out in an oxygen atmosphere at room temperature. In a typical experiment, alcohol (1 mmol), $L^{APIP}Cu^{II}$ (0.024 g, 4 mol-%), and KOH (0.560 g,

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1 mmol) were stirred in oxygen-saturated acetonitrile (5 mL) in a 10 mL two-neck round-bottom flask equipped with an oxygen balloon. The solution was stirred for 4–24 h according to the corresponding alcohol.

At appropriate intervals, 0.5 mL of reaction mixture was withdrawn and neutralized by addition of a drop of HCl (10% w/v) and distilled water (1 mL), and then extracted by dichloromethane or ethyl acetate. The organic phase was dried with anhydrous sodium sulfate and, after filtration, analyzed by gas chromatographic analyses.

The turnover number (TON) was determined as the number of mol of product per mol of complex. In a standardized TON experimental set up, to a mixture of benzyl alcohol (2M, 1 mL) and KOH (1 m, 0.28 g) in anhydrous CH_3CN (5 mL) was added the complex (2 mM, 0.005 g). The reaction mixture was stirred at ambient temperature under an oxygen balloon (1 bar) and the formation of benzaldehyde product with time was determined by taking samples at different time points. The oxidation process continues up to 6 h and then product formation saturates. The final organic products were quantitatively monitored by gas chromatographic analyses (as described above).

Calculations: Geometry optimizations were performed by using Gaussian 09 (revision D.01),^[35] the B3LYP functional,^[36] the TZVP basis set,^[37] and a polarized continuum model (PCM) for CH₂Cl₂ (dielectric $\varepsilon = 8.94$).^[38] Broken-symmetry^[39] (BS) DFT calculations were performed with the same functional and basis sets. Frequency calculations at the same level of theory confirmed that the optimized structures were located at a minimum on the potential energy surface.

CCDC-1004375 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Supporting Information (see footnote on the first page of this article): DFT-computed metrical parameters, cyclic voltammograms.

Acknowledgments

E. S. gratefully acknowledges the support by the Institute for Advanced Studies in Basic Sciences (IASBS) Research Council under grant G2014IASBS127. T. S. acknowledges an NSERC Discovery Grant. Westgrid and Compute Canada are thanked for access to computational resources.

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Received: July 21, 2014 Published Online: ■ Date: 11-11-14 14:08:23

Pages: 10



Ligand Design

Z. Alaji, E. Safaei,* L. Chiang, R. M. Clarke, C. Mu, T. Storr* 1–10

A Copper Complex of a Noninnocent Iminophenol-Amidopyridine Hybrid Ligand: Synthesis, Characterization, and Aerobic Alcohol Oxidation

Keywords: Ligand design / Biomimetic synthesis / Copper / Homogeneous catalysis / Oxidation



A new copper complex of a noninnocent iminophenol-pyridine hybrid ligand that is capable of efficient aerobic alcohol oxidation was studied.