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Effects of Charged Ligand Substituents on the Properties of the Formally Copper(III)-Hydroxide ([CuOH]²⁺) Unit

Debanjan Dhar,[†][©] Gereon M. Yee,[†][©] and William B. Tolman^{*}[©]

Department of Chemistry, Washington University in St. Louis, Campus Box 1134, 1 Brookings Drive, St. Louis, Missouri 63130, United States

Supporting Information

ABSTRACT: With the goal of understanding how distal charge influences the properties and hydrogen atom transfer (HAT) reactivity of the [CuOH]²⁺ core proposed to be important in oxidation catalysis, the complexes $[M]_3[^{SO3}LCuOH]$ (M = $[K(18-crown-6)]^+$ or $[K(crypt-222)]^+$) and $[^{NMe3}LCuOH]X$ (X = BAr_4^{F-1} or ClO_4^{-}) were prepared, in which SO_3^{-} or NMe_3^{+} substituents occupy the para positions of the flanking aryl rings of the supporting bis(carboxamide)pyridine ligands. Structural and spectroscopic characterization showed that the [CuOH]⁺ cores in the corresponding complexes were similar, but cyclic voltammetry revealed the $E_{1/2}$ value for the $[CuOH]^{2+}/[CuOH]^+$ couple to be nearly 0.3 V more oxidizing for the $[^{NMe3}LCuOH]^{2+}$ than the $[^{SO3}LCuOH]^-$ species, with the latter influenced by interactions between the distal $-SO_3^-$ substituents



and K⁺ or Na⁺ counterions. Chemical oxidations of the complexes generated the corresponding $[CuOH]^{2+}$ species as evinced by UV-vis spectroscopy. The rates of HAT reactions of these species with 9,10-dihydroanthracene to yield the corresponding $[Cu(OH_3)]^{2+}$ complexes and anthracene were measured, and the thermodynamics of the processes were evaluated via determination of the bond dissociation enthalpies (BDEs) of the product O–H bonds. The HAT rate for $[^{SO3}LCuOH]^-$ was found to be ~150 times faster than that for $[^{NMe3}LCuOH]^{2+}$, despite finding approximately the same BDEs for the product O– H bonds. Rationales for these observations and new insights into the roles of supporting ligand attributes on the properties of the [CuOH]²⁺ unit are presented.

INTRODUCTION

Among the myriad high-valent copper-oxygen motifs implicated with relevance to catalytic oxidations in biological and synthetic systems,¹ the recently characterized mononuclear [CuOH]²⁺ core (formally copper(III)-hydroxide) stands out as an excellent hydrogen atom abstraction reagent from a wide range of substrates.²⁻⁵ The ability of the [CuOH]²⁺ unit to activate robust C-H bonds has led to it being postulated as a potential intermediate in oxygenase enzymes, such as lytic polysaccharide monooxygenase.^{3,6} In previous work, the effects of ligand electronic perturbations on the spectroscopy and hydrogen atom transfer (HAT) reactivity of the [CuOH]²⁺ core were examined through comparison of complexes supported by the ligands shown in Figure 1.4,5 A conclusion drawn from these studies was that, in general, making the supporting ligand framework more electron-deficient makes the resulting copper hydroxide moiety a stronger oxidant but also a weaker base. These effects offset each other in defining the O-H bond dissociation enthalpy (BDE) of the Cu(II)aqua ($[CuOH_2]^{2+}$) product of HAT, but only partially, such that the complex with the highest $[CuOH]^{2+/+}$ redox potential exhibits the highest HAT thermodynamic driving force (BDE trend ^{NO2}LCu(OH₂) (**3b**) > ^{pyr}LCu(OH₂) (**3a**) > ^{pip}LCu-



Figure 1. Previously studied hydroxo/aqua complexes supported by indicated ligands (in box). R = Et or Bu.

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 (OH_2) (3c)). A similar trend in rates of HAT from dihydroanthracene by the corresponding $[CuOH]^{2+}$ cores was observed ($^{NO2}LCuOH$ (2b) > $^{pyr}LCuOH$ (2a) > $^{pip}L-CuOH$ (2c)), consistent with an Evans–Polanyi correlation, as seen with many other metal-oxo/hydroxo complexes.⁴

Inspired by the results of the studies performed using ligands of the same overall charge but differing electron donating abilities, we sought to explore the effects of varying the overall charge in the complexes by using ligands with either cationic $(-NMe_3^+)$ or anionic $(-SO_3^-)$ substituents. The installation of such charged distal residues is intended to mimic the effects of distally located charged protein residues on the hydrophobic active site of metalloenzymes and to probe how such secondary sphere effects alter reactivity patterns within the active site.⁷ Additionally, these charged residues would render the corresponding complexes to be soluble in water, a solvent of interest for several applications. Such a strategy of incorporating charged ligand substituents has been particularly well-explored in the porphyrin literature, often focusing on the use of cationic groups in the meso positions to give enhanced redox and HAT reactivity for metal-oxygen intermediates, as well as imbuing water solubility.⁸ It is also worth noting that attachment of cationic alkylammonium groups has significant effects on the rates of catalytic copolymerization reactions.⁹ Analogous examples featuring anionic substituents include one in which sulfonate-substituted phenyl groups at the meso positions of a heme-iron system influence both the oxidation potential of the porphyrin ring as well as the pK_a values of the corresponding iron(III)-bisaqua complexes when studied in water.¹⁰ Additional reports implicate the Lewis basicity of the pendant sulfonate functionalities as key determinants in altering reactivity by means of secondary coordination sphere effects.

With the aforementioned studies as precedents, we hypothesized that charged ligand substituents could have significant effects on the spectroscopic properties and reactivity of the $[CuOH]^{2+}$ core. Thus, we targeted new complexes of the proligands $[^{NMe3}LH_2]^{2+}$ and $[^{SO3}LH_2]^{2-}$ (Scheme 1) having $-NMe_3^+$ and $-SO_3^-$ groups on the *para* position of the carboxamide aryl rings. Herein, we describe the successful preparation and characterization of the proligands, their precursor complexes with the $[CuOH]^+$ unit, and the products of their one-electron oxidation comprising the $[CuOH]^{2+}$ core. The effects of the charged substituents on the properties of compounds are explored, leading to new understanding of how the supporting ligand environment influences the spectroscopic features and HAT kinetics and thermodynamics of the $[CuOH]^{2+}$ core.

RESULTS

Synthesis and Characterization of Ligands and Copper(II) Complexes. The proligands $[^{SO3}LH_2]^{2-}$ and $[^{NMe3}LH_2]^{2+}$, isolated as their respective ammonium and triflate salts, were synthesized as outlined in Scheme 1 (details in Supporting Information). In both cases, treatment of 2,6-pyridinedicarbonyl dichloride with 2 equiv of the corresponding aniline (or anilinium salt in the case of $[^{SO3}LH_2]^{2-}$) in the presence of excess base resulted in the formation of the dicarboxamide products $[(iPr)_2EtNH]_2[^{SO3}LH_2]$ and $^{NMe2}LH_2$ in gram quantities. Further treatment of $^{NMe2}LH_2$ with 2 equiv of MeOTf led to the rapid formation of $[^{NMe3}LH_2][OTf]_2$. Both ligand salts were characterized by ¹H and ¹³C{¹H} NMR spectroscopy and elemental analyses (Figures S1–S8). The





presence of the triflate anion in $[^{NMe3}LH_2][OTf]_2$ was confirmed from the $^{13}C\{^{1}H\}$ and ^{19}F NMR spectra (Figures S3 and S4). Also, $[(iPr)_2EtNH]_2[^{SO3}LH_2]$ was characterized structurally by X-ray crystallography (Figure S11). The X-ray crystal structure confirmed the overall formulation, with the acidic N–H proton on the countercation involved in a hydrogen-bonding interaction with one of the oxygen atoms of the sulfonate group (N–H–O distance ~2.8 Å and N–H–O bond angle 166.6°).¹²

The copper(II) hydroxide precursor complexes $[M]_3[^{SO3}LCuOH]$ (4a: $M = [K(18\text{-}crown-6)]^+$, 4b: $M = [K(crypt-222)]^+$) and $[^{NMe3}LCuOH]X$ (5a: $X = BAr^F_4^-$, 5b: $X = ClO_4^-$) were prepared by treatment of the proligand salts with 1 equiv of Cu(OTf)₂ under aqueous conditions in the presence of excess hydroxide (Scheme 2). In the case of $[K(18\text{-}crown-6)]_3[^{SO3}LCuOH]$ (4a), a crude solid was initially precipitated from the concentrated aqueous reaction mixture by the addition of acetone; subsequent trituration by tetrahydrofuran (THF) in the presence of excess 18-crown-6 yielded 4a as a blue solid (0.210 g, 58.0%). Elemental analysis

Scheme 2. Synthesis of Copper(II) Hydroxide Precursor Complexes



and X-ray crystallography (see below) support the indicated formulation. Further treatment of a solution of 4a in 1,2difluorobenzene (DFB) with 5 equiv of crypt-222, followed by recrystallization by vapor diffusion of Et₂O, yielded blue crystals of [K(crypt-222)]₃[^{SO3}LCuOH] (4b, 0.105 g, 87.0%). The complex $[^{NMe3}LCuOH]BAr^{F_4}$ (5a) was synthesized by the addition of 1 equiv of NaBAr^F₄ to the initial reaction mixture (proligand, base, $Cu(OTf)_2$), followed by extraction of the aqueous layer with CH2Cl2 and subsequent removal of the organic solvent to yield 5a as a light purple solid (0.149 g, 57.9%), the formulation of which was supported by elemental analysis. Attempts to structurally characterize 5a were unsuccessful, however, so the variant [NMe3LCuOH]ClO4 (5b) was prepared by slow evaporation of the aqueous reaction mixture in the presence of excess NaClO₄, giving crystals suitable for X-ray diffraction.

Anticipating that $[Cu(OH_2)]^{2+}$ cores would form as products of HAT by the $[CuOH]^{2+}$ complexes of $^{NMe3}L^{2-}$ and $^{SO3}L^{4-}$, we sought to prepare these aqua complexes independently. Success was achieved in the case of the former ligand, with $[^{NMe3}LCu(OH_2)](ClO_4)_2$ (6, 0.0784 g, 37.0%) isolated from the reaction of $[^{NMe3}LH_2][OTf]_2$, Cu(OTf)₂, and NaClO₄ in H₂O (a BAr^F₄⁻ salt was not accessible). The complex crystallizes as a hydrate, as determined by X-ray crystallography and elemental analysis. Similar attempts to synthesize a $[Cu(OH_2)]^{2+}$ complex for $^{SO3}L^{4-}$ led instead to the isolation of a dimer $[(Et_4N)_2(^{SO3}LCu)]_2$ (7, 0.120 g, S6.0%), in which the fourth coordination site of the copper center was found by X-ray crystallography to be occupied by one of the pendant sulfonate groups from a neighboring $[^{SO3}LCu]^{2-}$ unit (see below).

X-ray Crystal Structures. The X-ray structures of the [CuOH]⁺ complexes [M]₃[^{SO3}LCuOH] (4a: M = K(18crown-6), 4b: M = K(crypt-222)) and [^{NMe3}LCuOH]ClO₄ (**5b**) are depicted in Figure 2 (complexes only) and Figures 3 and 4 (including secondary interactions). Selected bond metrics are provided in Table 1, along with data for the previously reported complexes [Bu₄N][^{pyr}LCuOH] (1a), [Et₄N][^{NO2}LCuOH] (1b), and [Na][^{pip}LCuOH] (1c) for comparison.^{4,14} The geometric parameters for the primary copper coordination sphere for the set of complexes are similar, with average Cu1-N1/N3, Cu1-N2, and Cu1-O3 distances of 2.01, 1.93, and 1.85 Å, respectively. The complexes also exhibit closely analogous square-planar geometries characterized by similar τ_4 values of ~0.15.¹³ Thus, despite differences in remote substituents, overall charge, and/or outer-sphere interactions (see below), the structural features of the cores in the entire set of complexes are not significantly perturbed.

Secondary sphere interactions between the sulfonate and ligand carboxamide groups and the K^+ ion(s) are apparent in the structures of **4a** and **4b** (Figures 3 and 4, respectively). In **4a**, two K^+ centers bind to the oxygen atoms ($K \cdots O \approx 2.8$ Å) of the sulfonate groups (and reside within 18-crown-6 macrocycles),¹⁵ with the third bridging between ligand carboxamide oxygens in adjacent complexes (also within an 18-crown-6 molecule). The latter bridges thus result in the formation of a coordination network in the crystal (Figure 3, bottom). Such interactions with K^+ highlight the Lewis basic nature of the SO₃⁻ functionality. In the case of **4b**, the more effective encapsulation of the $[K(crypt-222)]^+$ counterions do not exhibit any significant secondary interactions (Figure 4,



Figure 2. Depictions of the X-ray crystal structures of the anionic portion of $[K(18\text{-}crown-6)]_3[^{SO3}LCuOH]$ (4a, top) and cationic portion of $[^{NMe3}LCuOH]ClO_4$ (5b, bottom). Gray, white, red, blue, green, and yellow atoms represent C, H, O, N, Cu, and S, respectively. H atoms are omitted for clarity, and non-hydrogen atoms are depicted as 50% thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows. 4a: Cu1–O3, 1.829(4); Cu1–N1, 1.996(4); Cu1–N2, 1.915(4); Cu1–N3, 2.012(4); N1–Cu1–N3, 159.7(2); N2–Cu1–O3, 179.3(2). 5b: Cu1–O3, 1.862(2); Cu1–N1, 2.015(2); Cu1–N2, 1.932(2); Cu1–N3, 2.008(2); N1–Cu1–N3, 159.4(1); N2–Cu1–O3, 176.5(1).

top). Notwithstanding what would be expected to be coordinative saturation by the multidentate cryptand ligand, the third $[K(crypt-222)]^+$ cation exhibits a bonding interaction with one of the pendant SO_3^- groups on the ligand framework (Figure 4, bottom). This interaction is indicated by disorder of the central K^+ ion, with a 15% disordered component (K3') sitting outside the central cryptand cavity and involved in an ionic interaction with the SO₃⁻ in a similar bidentate fashion as observed in 4a (K3'-O4, 2.781(15) Å; K3'-O6, 2.842(14) Å). Evidently, the SO_3^- moiety binds strongly enough to the K⁺ ion to cause it to be partially dislodged from the rigid, tightly coordinating cryptand cavity. As noted below, the strong tendency for the sulfonate unit to be involved in secondary interactions with K⁺ as identified in the crystalline phase is important in solution as well, with implications for certain properties and reactivity.

The X-ray structure of the aqua complex [$^{NMe3}LCu(OH_2)$]-(ClO₄)₂ (**6**) is shown in Figure S12. The cationic unit closely resembles that in [$^{NMe3}LCuOH$]ClO₄ (**5b**), with the exception of a Cu–O distance of 1.927(2) Å, which is 0.065 Å longer than that in **5b**, consistent with an aqua ligand in **6**. The aqua ligand hydrogen atoms appear to be hydrogen-bonded to water solvate molecule(s), but these are disordered such that details of the interactions are unclear. Finally, the X-ray structure of [(Et₄N)₂(^{SO3}LCu)]₂ (7) reveals it to be a dimer with sulfonate from one unit binding to the Cu(II) ion of the other (Figure 5). The S–O bond distance for the oxygen atom in the sulfonate that is coordinated to the Cu(II) ion is longer, measuring 1.483(2) Å as opposed to ~1.44 Å in the other S–



Figure 3. Additional views of the X-ray crystal structure of $[K(18-crown-6)]_3[^{SO3}LCuOH]$ (**4a**) with non-hydrogen atoms depicted as 50% thermal ellipsoids, highlighting the interactions with the $[K(18-crown-6)]^+$ units. Hydrogen atoms are omitted for clarity. Gray, white, red, blue, green, yellow, and purple atoms represent C, H, O, N, Cu, S, and K, respectively. (top) View of the three $[K(18-crown-6)]^+$ units associated with each anion. (bottom) The coordination polymer network in the solid-state structure depicting the repeating units (faded) and the key coordinating components (highlighted).



Figure 4. Depiction of the X-ray crystal structure of $[K(crypt-222)]_3[^{SO3}LCuOH]$ (4b), showing the anionic portion and the $[K(crypt-222)]^+$ unit that interacts with the sulfonate group. Gray, white, red, blue, green, yellow, and purple atoms represent C, H, O, N, Cu, S, and K, respectively. Hydrogen atoms are omitted for clarity, and the non-hydrogen atoms are shown as 50% thermal ellipsoids. Both disordered K⁺ centers are shown (occupancies: K3, 85%; K3', 15%).

O bonds in the sulfonate. Such asymmetry in coordinated sulfonates has been reported previously in the literature.¹⁶

UV-Vis and EPR Spectroscopy. Despite their different overall charges, the electronic structures of the copper(II)

Table 1. Comparison of Selected Interatomic Distances	(Å)
for [CuOH] ⁺ Complexes ^{<i>a</i>}	

compound	Cu1-OH	Cu1-N2	Cu1-N1/N3	$\tau_4^{\ b}$
[K(18-crown- 6)] ₃ [^{SO3} LCuOH] (4a)	1.829(4)	1.915(4)	1.996(4), 2.012(4)	0.16
[K(crypt- 222)] ₃ [^{SO3} LCuOH] (4b)	1.848(3)	1.937(3)	2.006(3), 2.012(3)	0.15
$[^{\rm NMe3}LCuOH]ClO_4 (5b)$	1.862(2)	1.932(2)	2.015(2), 2.008(2)	0.17
[Bu ₄ N][^{pyr} LCuOH] (1a) ^b	1.845(4)	1.924(3)	2.016(3), 2019(3)	0.16
	1.859(2)	1.936(2)	2.005(1), 1.998(1)	0.17
$[Na][^{pip}LCuOH] (1c)^{c,d}$	1.885(2)	2.032(3)	1.958(3), 1.963(3)	0.20
	1.891(2)	2.035(3)	1.959(3), 1.948(3)	0.18

^{*a*}Estimated standard deviations are indicated in parentheses. ^{*b*}Reference 14. ^{*c*}From ref 4. ^{*d*}Two molecules in the asymmetric unit, Na⁺ is coordinated to the hydroxide.



Figure 5. Depiction of the anionic portion of the X-ray crystal structure of $[(Et_4N)_2({}^{SO3}LCu)]_2$ (7), with non-hydrogen atoms depicted as 50% thermal ellipsoids and H atoms omitted for clarity. Gray, blue, red, green, and yellow atoms represent C, N, O, Cu, and S, respectively. Selected interatomic distances (Å) and angles (deg) are as follows: Cu1–O3, 1.9445(19); Cu1–N1, 1.928(2); Cu1–N2, 1.995(2); Cu1–N3, 1.995(2); S1–O3, 1.483(2); N2–Cu1–N3, 160.63(10); N1–Cu1–O3, 173.93(10).

cores in $[K(18\text{-}crown-6)]_3[^{SO3}LCuOH]$ (4a), $[^{NMe3}LCuOH]$ -BAr^F₄ (5a), and $[Bu_4N][^{pyr}LCuOH]$ (1a) appear to be essentially identical on the basis of UV–vis and electron paramagnetic (EPR) spectroscopy (Figure 6).^{4,17} Thus, overlay of the UV–vis (DFB) and EPR spectra (THF or 1:4 DFB/ THF) for 4a, 5a, and 1a reveals closely similar features (EPR parameters from simulations provided in Tables S1 and S2). The similarities are also evident in spectra measured of aqueous solutions of 4a and 5b (Figures S15 and S16), although the superhyperfine coupling from the N atoms is largely unresolved, consistent with the known line-broadening effects of solvent water.¹⁸

Cyclic Voltammetry. While the *para*-SO₃⁻ and -NMe₃⁺ substituents have little effect on the UV–vis and EPR spectroscopic features of [K(18-crown-6)]₃[^{SO3}LCuOH] (4a) and [^{NMe3}LCuOH]BAr^F₄ (5a), the charged residues dramatically influence their electrochemical behavior. Cyclic voltammetry measurements made in DFB solvent¹⁹ (Figure 7, Table 2) revealed quasi-reversible single-electron redox events with $E_{1/2}$ values of -0.135 and 0.140 V (vs Fc⁺/Fc) for [K(18-crown-6)]₃[^{SO3}LCuOH] (4a) and [^{NMe3}LCuOH]BAr^F₄ (5a), respectively. The shown cyclic voltammogram (CV) of the parent complex [Bu₄N][^{pyr}LCuOH] (1a) ($E_{1/2} = -0.076$ V),



Figure 6. (top) Overlay of UV–vis spectra for **4a**, **5a**, and **1a** taken in DFB at 298 K. (bottom) Overlay of EPR spectra of **4a** (1:4 by volume DFB/THF), **5a** (THF), and **1a** (THF) at 30 K.

in combination with the previously reported data for $[\text{Et}_4\text{N}][^{\text{NO2}}\text{LCuOH}]$ (**1b**; $E_{1/2} = 0.124$ V) and $[\text{Bu}_4\text{N}]-[^{\text{pip}}\text{LCuOH}]$ (**1c**; $E_{1/2} = -0.260$ V),^{3,4} serve as precedent for assignment of the waves for **4a** and **5a** as analogous $[\text{CuOH}]^{2+}/[\text{CuOH}]^+$ couples. As expected, the electron-withdrawing properties of the NMe₃⁺ substituents in **5a** ($\sigma_p = 0.88$) result in a positively shifted redox potential, slightly larger than that seen for **1b** (NO₂ groups $\sigma_p = 0.78$).²⁰ On the contrary, while the $-\text{SO}_3^-$ substituents in **4a** are slightly electron-withdrawing in nature ($\sigma_p = 0.09$),²⁰ the redox potential is ~60 mV *lower* than that of the parent complex [Bu₄N][^{pyr}LCuOH] (**1a**). We surmise that this result reflects the overall trianionic nature of **4a**, which renders the one-electron oxidation thermodynamically more favorable.²¹

Effect of Counterions on the Spectroscopic and Electrochemical Properties of $[M]_3[^{SO3}LCuOH]$ (4a or 4b). In view of the secondary interactions between the K⁺ ions and the sulfonate groups observed by X-ray crystallography, we sought to understand the role of these interactions on the solutionstate spectroscopic and/or electrochemical properties of 4a or



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Figure 7. CVs of $[K(18\text{-}crown-6)]_3[^{SO3}LCuOH]$ (4a) (blue), $[^{NMe3}LCuOH]BAr_4^F$ (5a) (red), and $[Bu_4N][^{pyr}LCuOH]$ (1a) (black dotted). Conditions: 2 mM analyte in DFB solvent, 0.2 M Bu_4NPF_6 (0.2 M $Bu_4NBAr_4^F$ in case of 5a; data for this electrolyte provided in Figures S9 and S10).

Table 2. $E_{1/2}$ Values for the [CuOH]²⁺/[CuOH]⁺ Redox Couples of 4a, 5a, and $1a-c^a$

complex	$E_{1/2}$ (V vs Fc ⁺ /Fc)
$[K(18-crown-6)]_{3}[^{SO3}LCuOH] (4a)$	-0.135
$[^{\text{NMe3}}\text{LCuOH}]\text{BAr}^{F}_{4}]$ (5a)	0.140
$[NBu_4][^{pyr}LCuOH] (1a)^b$	-0.076
$[NBu_4][^{NO2}LCuOH] (1b)^b$	0.124
$[NBu_4][^{pip}LCuOH] (1c)^b$	-0.260
	,

^{*a*}Conditions: 2 mM analyte in DFB solvent, 0.2 M Bu_4NPF_6 (0.2 M $Bu_4NBAr_4^F$ in case of **5a**). ^{*b*}From ref 3.

4b. To probe such effects, 100 equiv of [Na(15-crown-5)]OTf were added to solutions of [K(18-crown-6)]₃[^{SO3}LCuOH] (4a) in DFB, which were analyzed by UV-vis and EPR spectroscopy, as well as cyclic voltammetry. The addition of [Na(15-crown-5)]OTf had little influence on the UV–vis and EPR spectra of 4a, with virtually no changes to the UV-vis spectrum (Figure S17) and only subtle shifts in the g_{\parallel} component of the EPR spectrum (Figure 8, top; Table S2 and Figure S14). In contrast, the electrochemical differences were stark, with the CV showing a large (~180 mV) positive shift in the $E_{1/2}$ for the $[CuOH]^{2+}/[CuOH]^{+}$ couple from -0.135 to 0.043 V (vs Fc⁺/Fc; Figure 8, bottom). A similar shift was also observed upon addition of [Na(15-crown-5)]OTf to [K(crypt-222)]₃[^{SO3}LCuOH] (4b) (Figures S13 and \$19; the CVs for 4a and 4b are essentially identical in water; see Figure S18). The magnitude of this shift to a higher potential by mere alteration of the counterion is comparable to the difference in the redox potentials between [Bu₄N]-[^{pyr}LCuOH] (1a) and [Et₄N][^{NO2}LCuOH] (1b) ($\Delta E_{1/2} \approx$ 200 mV).⁴ We interpret the results to suggest that there is a significant difference between the interactions of the pendant $-SO_3^-$ groups in 4a/4b with the K⁺-containing counterions compared to $[Na(15\text{-crown-}5)]^+$. While this difference causes significant changes in the redox potential, the UV-vis and EPR



Figure 8. (top) Overlay of EPR spectra of $[K(18\text{-crown-}6)]_3[^{SO3}LCuOH]$ (4a) both in the absence (black) and presence (blue) of 100 equiv of [Na(15-crown-5)]OTf. The dashed line shows the subtle difference in the g_z component (1 mM concentration of 4a in DFB). (bottom) Overlay of CVs for 4a in DFB in the absence (black) and presence (blue) of 100 equiv of [Na(15-crown-5)]OTf. Conditions: 2 mM analyte in DFB solvent, 0.2 M Bu₄NPF₆, 50 mV/s.

spectra are largely unaffected, reflecting little perturbation to the electronic structure of the copper ion itself. To rationalize the more positive $E_{1/2}$ in the presence of [Na(15-crown-5)]OTf, we hypothesize that in DFB solvent the Lewis basic $-SO_3^-$ group interacts more strongly with the more Lewis acidic Na⁺ ion²² and exists as a "tighter" ion pair, thus mitigating the electrostatic effect of the anionic $-SO_3^-$ groups (i.e., effectively decreasing the overall charge) and leading to an anodic shift in the [CuOH]²⁺/[CuOH]⁺ redox potential.

Characterization of [CuOH]²⁺**Complexes.** Treatment of solutions of $[K(18 \text{-} \text{crown-6})]_3[^{\text{SO3}}\text{LCuOH}]$ (4a) and $[^{\text{NMe3}}\text{LCuOH}]\text{BAr}^F_4$ (5a) in DFB with 1 equiv of oxidant ([Fc]BAr}^F_4 for 4a; [AcFc]BAr}^F_4 for 5a) at -25 °C resulted in the immediate formation of intense features in the corresponding UV-vis spectra (Scheme 3, Figure 9).²³ By analogy to



Figure 9. Overlay of UV-vis spectra. Red (solid line): $[K(18\text{-crown-6})]_2[^{SO3}LCuOH]$ (8a); blue: $[^{NMe3}LCuOH](BAr^F_4)_2$ (9a); black (dotted): $^{NO2}LCuOH$ (2b); red (dashed): $[K(18\text{-crown-6})]_2[^{SO3}LCuOH]$ + 100 equiv of [Na(15-crown-5)]OTf (8a').

results of previous studies, we attribute these features to ligand aryl π to Cu $d_{x^2-y^2}$ charge transfer transitions of the [CuOH]²⁺ cores in the product complexes [K(18-crown-6)]₂[^{SO3}LCuOH] (8a) and [^{NMe3}LCuOH](BAr^F₄)₂ (9a), respectively. The broad absorption feature for [K(18-crown-6)]₂[^{SO3}LCuOH] (8a; solid red line, Figure 8) at ~610 nm (ε = 12 500 M⁻¹ cm⁻¹) is significantly red-shifted relative to the sharper feature for [^{NMe3}LCuOH](BAr^F₄)₂ (9a; solid blue line) centered around ~498 nm (ε = 14 000 M⁻¹ cm⁻¹). The latter spectrum is quite similar to that reported previously for ^{NO2}LCuOH (2b; dashed black line) (λ_{max} (ε) = 513 nm (15 000 M⁻¹ cm⁻¹)), with respect to both peak shape and position, attesting to similar electron-withdrawing effects of the -NO₂ and -NMe₃⁺ substituents.⁴ For the oxidation reactions of

4a and 5a, titration experiments revealed a 1:1 reaction stoichiometry (Figures S20 and S21), confirming that oxidation of the copper(II) hydroxide precursor proceeds cleanly via a one-electron process. The absorption bands for the oxidized products decay fully within 2–3 h at –25 °C and immediately upon warming. Additionally, the rates of decay at lower temperatures are enhanced upon the addition of external substrates containing C–H bonds that can be activated (see below). These observations are consistent with prior characterization of analogous [CuOH]²⁺ complexes.^{3,4}

In line with the electrochemical measurements discussed above, the chemical oxidation of [K(18-crown-6)]₃[^{SO3}LCuOH] (4a) also was found to be sensitive to the nature of the countercation. In the presence of [Na(15-crown-5)]OTf (100 equiv), the reaction of 4a with $[Fc]BAr_4^F$ did not proceed to give 8a as shown above. Conversion to 8a' instead required the use of the stronger oxidant [AcFc]BAr^F₄ ($E_{1/2} \approx$ 0.27 V vs Fc^+/Fc ,²⁴ with the product exhibiting a UV-vis spectrum with slightly different features from those of 8a (Figure 9, Figure S22). Interestingly, the analogous spectrum can be generated by treating a solution of 8a (generated using $[AcFc]BAr^{F}_{4}$ with an excess (>5.0 equiv) of [Na(15-crown-5)]OTf (Figure S23). This behavior is consistent with the observed shift in $E_{1/2}$ in the presence of [Na(15-crown-5)]OTf (Figure 8, bottom). We speculate that the subtle difference between the observed ligand-to-metal charge transfer (LMCT) features in the presence or absence of [Na(15-crown-5)]OTf is a consequence of different interactions between the pendant sulfonates and the Na⁺/K⁺ counterions, which result in subtle electronic perturbations to the highest occupied molecular orbital (HOMO) known to have significant ligand π character.^{2,4} The larger red shifts of the UV-vis features for $[M(18\text{-crown-6})]_2[^{SO3}LCuOH]$ (8a, M = Na or K) relative to those of $[^{NMe3}LCuOH](BAr^{F}_{4})_{2}$ (9a) also are consistent with the expected effects on the ligand-centered HOMO (more electron-withdrawing -NMe₃⁺ substituent increases energy of ligand $\pi \to \text{Cu } d_{x^2-y^2}$ LMCT transition).

Determination of O-H BDEs. As in the previous work,⁴ we sought to understand the influence of the ligand-based electronic perturbations on the HAT reactivity of the new [CuOH]^{2+⁻} complexes. A measure of the thermodynamic driving force for abstraction of H atoms by the complexes with [CuOH]²⁺ cores is the bond dissociation enthalpy of the O–H bond in the product $[Cu(OH_2)]^{2+}$ unit.³ In previous work, two methods for determining this value for the products 3a-c (Figure 1) of the HAT reactions of 2a-c were used.^{3,4} One method involved use of a thermodynamic square scheme, whereby values for the [CuOH]^{2+/1+} reduction potential and the pK_a for the $[Cu(OH_2)]^{2+}$ complex were inserted into eq 1 (where $C_{\rm H}$ is associated with the H⁺/H· standard reduction potential in the solvent used, which was THF). A second method ("cross-HAT") involved mixing of a [CuOH]²⁺ complex supported by one ligand (L) with the $[{\rm Cu}({\rm OH}_2)]^{2+}$ complex of another (L') and measuring the K_{eq} for the resulting equilibrium expressed by Scheme 4. The difference in the BDE values (Δ BDE) between the two [Cu(OH₂)]²⁺ cores may then be approximated by $-RT \ln K_{eq}$, under the assumption that ΔS_{rxn} is negligible and ΔH_{rxn} is independent of temperature. We considered both methods in seeking to determine the BDE values for the $[Cu(OH_2)]^{2+}$ cores supported by ^{NMe3}L and ^{SO3}L⁴⁻ and to compare them to the values previously determined for 3a-c.

Scheme 4. Equilibrium Measured to Determine the ΔBDE between $[Cu(OH_2)]^{2+}$ Cores

$$[LCuOH]^{n+} + [L'Cu(OH_2)]^{n+}$$
$$\iint K_{eq}$$
$$[LCu(OH_2)]^{n+} + [L'CuOH]^{n+}$$

BDE (kcal mol⁻¹) = 1.37 pK_a + 23.06 $E^{\circ} + C_{\rm H}$ (1)

Thus, [K(18-crown-6)]₂[^{SO3}LCuOH] (8a) was generated by reaction of $[K(18-crown-6)]_3[^{SO3}LCuOH]$ (4a) with $[Fc]BAr_{4}^{F}$ (1 equiv) in DFB at -25 °C and then treated with varying amounts of the parent aqua complex pyrLCu- (OH_2) (3a, 0.25–2.50 equiv).² Monitoring this reaction by UV-vis spectroscopy showed decay of 8a and concomitant conversion of aqua complex 3a to pyrLCuOH (2a) until equilibrium was reached, as evinced by cessation of change in the UV-vis spectrum (Figure S24). Deconvolution of the equilibrium spectrum by multicomponent fitting enabled determination of the equilibrium constant $K_{eq} = 4.2 \pm 1.8$ (illustrative deconvolution traces shown in Figure S25), corresponding to a \triangle BDE of ~0.8 kcal mol⁻¹, such that the O-H BDE for $[K(18\text{-crown-6})]_2[^{SO3}LCu(OH_2)]$ (10a) is ~0.8 kcal mol⁻¹ stronger than that for 3a (90 \pm 3 kcal mol⁻¹; Table 3).³

Table 3.	BDE	Values	for	$[CuOH_2]^{2+}$	Complexes
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supporting ligand	solvent	BDE (kcal/mol)	ref		
^{SO3} L ⁴⁻	DFB	~91 ^{<i>a</i>}	this work		
	H_2O	~87	this work		
NMe3L	DFB	~91.5 ^{<i>a</i>}	this work		
	H_2O	~91	this work		
pyrL ²⁻	THF	90 ± 3	4		
NO2L2-	DFB	91 ± 3	4		
pipL ²⁻	THF	88 ± 3	4		
^a Approximate value, see text.					

Unfortunately, the cross-HAT protocol proved unsuitable for determining the O–H BDE of $[^{\rm NMe3}LCu(OH_2)](BAr^F_4)_2$ (6a), the product of HAT by $[^{\rm NMe3}LCuOH](BAr^F_4)_2$ (9a), owing to difficulties in reproducibly determining the point of equilibrium. However, addition of an excess of $[^{\rm pyr}LCu(OH_2)]$ (3a, 2.5 equiv) to a solution of 9a (generated by oxidation of 5a with 1 equiv of $[AcFc]BAr^F_4$ in DFB solvent at -25 °C) resulted in the complete conversion of 3a to $^{\rm pyr}LCuOH$ (2a) within ~2 min (Figure S26). Assuming ~95% conversion of 3a of 2a, we estimate the $K_{\rm eq}$ for this reaction to be ~11, which gives a Δ BDE between 3a and 6a of ~1.5 kcal mol⁻¹, such that the O–H bond of the latter is stronger than that of the former. Thus, the O–H BDE for complex 6a is estimated to be ~91.5 kcal mol⁻¹ (Table 3).

To further validate the results from the cross-HAT experiments, we took advantage of the water solubility of $[K(18\text{-}crown\text{-}6)]_3[^{SO3}LCuOH]$ (4a) and $[^{NMe3}LCuOH]ClO_4$ (5b) to more directly evaluate the BDE of the O-H bonds in $[K(18\text{-}crown\text{-}6)]_2[^{SO3}LCu(OH_2)]$ (10a) and $[^{NMe3}LCu-(OH_2)](ClO_4)_2$ (6b) using eq 1, where $C_H = 55.8$ kcal mol^{-1.25} The pK_a of 10a was determined through UV-vis titrations of 4a dissolved in water, by varying the pH between 4.75 and 11.35, where the pH was adjusted by using either KOH or HClO₄ and measured using a pH probe (Figure S27,

Table 4. Thermodynamic	and Kinetic Data for HAT	T Reactions of [CuOH] ²	²⁺ Complexes with 9,10-Dihy	ydroanthracene (DHA)
and 1,4-Cyclohexadiene (CHD) at -25 °C in DFF	3		

compound	ligand	$\Delta \text{BDE}_{\text{DHA}} \ (\text{kcal mol}^{-1})^a$	$k_{\rm DHA}~({ m M}^{-1}~{ m s}^{-1})$	$k_{\rm H}/k_{\rm D}$ (DHA)	$k_{\rm CHD} \ ({ m M}^{-1} \ { m s}^{-1})$	$\Delta \mathrm{BDE}_{\mathrm{CHD}} \ (\mathrm{kcal} \ \mathrm{mol}^{-1})^a$
8a	SO3L4-	14.7	400(22)	12	70(8)	15
8a' ^b	SO3L4-	14.7	500(30)	-	90(9)	15
9a	^{NMe3} L	14.7	2.8(7)	18 ^c	28(2)	15
$2a^d$	pyrL ²⁻	13.7	50(8)	27 ^e	$38(2)^{f}$	14
$2\mathbf{b}^d$	$^{NO2}L^{2-}$	14.7	346(50)	10 ^e	-	15
$2c^d$	pipL2-	11.7	25(4)	17 ^e	-	12

^{*a*}Calculated as the difference between the O–H BDE of the product $[Cu(OH_2)]^{2+}$ complex and the BDE of the substrate C–H bond (taken from ref 30). ^{*b*}100 eq. of [Na(15-crown-5)]OTf added. ^{*c*}For this value k_D is taken as the average of the k_D values measured at 243 and 253 K (see Figure S33). ^{*d*}From ref 4 unless otherwise stated. ^{*e*}Extrapolated values, determined from activation parameters reported in ref 4 measured in CH₂Cl₂. ^{*f*}From ref 31.

left).²⁶ The intermediate equilibrium spectra were deconvoluted into the proportions of **10a** and **4a** via multicomponent fitting, using the two-component spectra measured at pH 4.75 (**10a**) and pH 11.35 (**4a**).²⁷ With these proportions and the measured pH of the solution at the equilibrium points, the pK_a of **10a** was found to be 10.1 ± 0.2 . In a similar fashion, the corresponding titration of **5b** in water also was followed by UV–vis spectroscopy and deconvoluted to obtain the pK_a of [^{NMe3}LCu(OH₂)](ClO₄)₂ (**6b**) as 8.0 ± 0.2 (Figure S27, right). Alternatively, for **5b** a standard pH titration curve was generated by measuring the pH with a pH probe (Figure S28), and a pK_a value of ~8.3 was obtained for **6b**, which is in reasonable agreement with the result obtained from the UV–vis titration.

Determination of the $E_{1/2}$ values in water for the oneelectron redox potentials corresponding to the 8a/4a and 9b/ 5b redox couples was achieved through cyclic voltammetry experiments performed at high pH to ensure full conversion to the hydroxide form during the experiment. This proved difficult in the case of the 8a/4a couple, owing to the significant overlap between the oxidative feature and the apparent onset of catalytic water oxidation under basic conditions.²⁸ Nevertheless, an approximate $E_{1/2} = 0.75$ V (vs normal hydrogen electrode (NHE)) was determined (Figure S29, left) at pH = 11. In the case of the 9b/5b redox couple, an $E_{1/2}$ = 1.03 V (vs NHE) was measured at pH = 14 (Figure S29, right). Thus, with these values, eq 1 gave O-H BDE values of ~87 and ~91 kcal mol⁻¹ for 10a and 6a/b, respectively (Table 3). While the BDE value for 10a is slightly lower than the BDE value of ~ 91 kcal mol⁻¹ determined from the nonaqueous cross-HAT measurements, it is well-within the range of O-H BDE values that have been seen thus far for $[Cu(OH_2)]^{2+}$ complexes.^{3,4,29} Importantly, the trend in O-H BDE values measured in both organic and aqueous media matches (6a/b >10a).

HAT Reaction Kinetics. To probe how the distal-charged substituents alter the HAT reaction kinetics of $[K(18\text{-crown-6})]_2[^{SO3}LCuOH]$ (**8a**) and $[^{NMe3}LCuOH](BAr^{F_4})_2$ (**9a**), we measured the rates for reactions of these complexes with 9,10-dihydroanthracene (DHA) and/or DHA- d_4 in DFB solvent at -25 °C. In the experiments, solutions of **4a** or **5a** in the presence of excess substrate were treated with the appropriate oxidant, which immediately yielded the diagnostic charge-transfer features associated with the formation of the corresponding $[CuOH]^{2+}$ species. This charge-transfer feature decayed over time, concomitant with the appearance of sharp absorption features in the 360–380 nm range, indicative of the formation of anthracene (Figures S30 and S31), the expected

organic product of the HAT reaction. The decays of the LMCT band were modeled with a single exponential function to obtain pseudo-first-order rate constants (k_{obs}) , and plots of these values versus substrate concentration (Figures S30–S33) yielded the second-order HAT rate constants (k). For comparison, we tabulate these rate constants and the corresponding kinetic isotope effect (KIE) values determined by using DHA- d_4 in Table 4 with those reported previously for the other [CuOH]²⁺ complexes **2a–c**.

Comparison of the second-order rate constants shows $[K(18\text{-}crown\text{-}6)]_2[^{SO3}LCuOH]$ (8a) to react most rapidly with DHA, with a rate constant similar to that measured for 2b supported by $^{NO2}L^{2-}$ and in line with the strong O–H BDE measured for 8a.⁴ Notably, the second-order rate constant measured for reaction with $[^{NMe3}LCuOH](BAr^F_4)_2$ (9a) is ~150 times less than that for 8a, despite having a similar thermodynamic driving force. It is also noteworthy that both 8a and 9a exhibit large kinetic isotope effects of 12 and 18 (at -25 °C; Figures S32 and S33). These large values are consistent with rate-determining C–H bond cleavage and are similar to those reported previously for the analogous $[CuOH]^{2+}$ complexes $2a-c.^{2,4}$

In assessing the possible reasons for the significantly slower reaction of 9a with DHA, we noted that the 2+ charge of the complex is balanced by the two large BAr_{4}^{F} counterions, which might crowd the [CuOH]²⁺ core and hinder reactivity with a sterically encumbered substrate such as DHA. To probe this hypothesis, we measured the second-order rate constant for reactions of 8a and 9a with 1,4-cyclohexadiene (CHD), a smaller hydrogen atom donor with a comparable C-H BDE to that of DHA (76.0 \pm 1.2 and 76.3, respectively), which typically undergoes HAT reactions at similar rates.^{30,31} Indeed, for 9a the reactions with CHD were found to be ~10 times faster than for DHA, with $k = 28(2) \text{ M}^{-1} \text{ s}^{-1}$ (Figure S34, right). This value is quite similar to what was previously measured for 2a ($k = 38 \text{ M}^{-1} \text{ s}^{-1}$) under analogous conditions.³¹ The value determined for 8a is also similar (70(8) $M^{-1} s^{-1}$; Figure S33), and it is smaller than the rate constant for its reaction with DHA. Taken together, the evidence supports the notion that the slow rate of reaction of 9a derives from steric hindrance by the bulky counterions.³²

Inspired by the observations that the nature of the counterion had a considerable effect on the redox potential for the $[CuOH]^{2+}/[CuOH]^+$ couple for 8a, we investigated the influence of counterions on its HAT reactivity. The reaction between DHA and 8a was repeated in the presence of 100 equiv of [Na(15-crown-5)]OTf and yielded a slightly larger second-order rate constant (k) of $500(30) \text{ M}^{-1} \text{ s}^{-1}$

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(Figure 10, Table 4). Concerned that changes in the ionic strength might affect the reaction rate,³³ we performed a



Figure 10. (top) Kinetics plots for the reaction between **8a** and DHA in the presence of 100 equiv of [Na(15-crown-5)]OTf (blue), 100 equiv of Bu_4NPF_6 (red), or no added electrolyte (black) in DFB at -25 °C. (bottom) Kinetics plots for the reaction between **9a** and DHA in the absence (black) and presence (red) of 100 equiv of $Bu_4NBAr_4^F$ in DFB at -25 °C.

control reaction of **8a** with DHA in the presence of 100 equiv of $[Bu_4N]PF_6$ (Figure 10). The observed rate constant in this case was found to be 300(12) $M^{-1} s^{-1}$, slightly *lower* than in the absence of added electrolyte, and consistent with the presence of ion pairing in **8a**.³⁴ Moreover, analogous reactions with **9a** performed in the presence of excess $[Bu_4N]BAr^F$ yielded no difference in the rate of HAT. Taken together, these data provide firm evidence for an intrinsic difference in the influence of the $[Na(15\text{-}crown-5)]^+$ and $[K(18\text{-}crown-6)]^+$ counterions on the HAT properties of the $[CuOH]^{2+}$ core, presumably resulting from divergent interactions between the Na⁺ and K⁺ ions and the sulfonate groups.

DISCUSSION

Using two new derivatives of the pyridine-dicarboxamide ligand L^{2-} having charged $-SO_3^-$ or $-NMe_3^+$ substituents, we prepared and characterized the Cu(II) hydroxide ([CuOH]⁺) complexes $[M]_3[^{SO3}LCuOH]$ (4a: M = $[K(18 \text{-crown-6})]^+$, 4b: $M = [K(crypt-222)]^+)$ and $[^{NMe3}LCuOH]X$ (5a: $X = BAr^F_4$, **5b**: $X = ClO_4^{-}$). A key question we wished to address was how the charged substituents influenced the properties of the [CuOH]⁺ cores and whether the nature of the electronic perturbation (resonance vs field effect) was an important factor. The X-ray structures showed little variation in the Cu(II) coordination geometries as a function of para substituent, but the presence of significant interactions between the $-SO_3^-$ groups and the K⁺ ions in the solid-state structures of 4a and 4b is an important feature in these complexes that has implications for their properties in solution. The tendency of the $-SO_3^-$ units to act as ligands was further illustrated in the X-ray structure of $[(Et_4N)_2^{(SO3}LCu)]_2$ (7), which was isolated in attempts to prepare a $[Cu(OH_2)]^2$ complex. UV–Vis and EPR spectra of the [CuOH]⁺ complexes 4 and 5 were closely analogous, indicative of similar electronic structures for the tetragonal Cu(II) compounds despite their different overall charges. In contrast, considerable differences in the redox potentials for the $[CuOH]^{2+}/[CuOH]^+$ couples were observed, which varied as a function of the supporting ligand substituents and, for the $-SO_3^-$ system, the nature of the countercation (Table 2). A plot of $E_{1/2}$ value as a function of Hammett parameter (σ_p) for the complexes supported by the pyridine-containing ligands shows a reasonable correlation (slope = +0.26) for the complexes bearing the $^{pyr}L^{2-}$, $^{NO2}L^{2-}$, and ^{NMe3}L ligands, but those featuring the ^{SO3}L²⁻ ligand with either K^+ or Na^+ counterions fall off the line (Figure 11a). We attribute this observation to the use of a single $\sigma_{\rm p}$ value for the $-SO_3^-$ group (reported from measurements in water)²⁰ that does not take into consideration the effects of interactions with countercations in aprotic organic solvents. That is, differences in the interactions with Na⁺ and K⁺ evidently induce disparities in the $E_{1/2}$ values by modulating the electron-withdrawing capabilities of the $-SO_3^-$ group.

As noted previously⁴ and reproduced in Figure 11b, the A_{z} value (which reflects spin localization on the Cu nucleus) varies linearly with $E_{1/2}$ value for the complexes supported by $^{pip}L^{2-}$, $^{pyr}L^{2-}$, and $^{NO2}L^{2-}$ (black circles). The data for the new ligands with $-NMe_3^+$ and $-SO_3^-$ substituents do not fit to this line, however. As noted above, the disparity for the ^{SO3}L⁴⁻ systems with Na⁺ and K⁺ countercations is likely due to ionic interactions that modulate the electron-withdrawing properties of the $-SO_3^-$ moiety. A different explanation is needed to rationalize the significant difference in A_z values for the $^{\rm NMe3}L$ system compared to that comprising ${}^{\rm NO2}\!\tilde{L}^{2-}$ that has similarly electron-withdrawing $-NO_2$ groups (with a similar σ_p value). We postulate different sensitivity of A_z to resonance and field effects that contribute to $\sigma_{\rm p}$, as it is known that the $-{\rm NO}_2$ and -NMe₃⁺ groups differ with respect to these effects.³⁵ Thus, we hypothesize that electron withdrawal via resonance is a significant contributor to a decreased A_z value and that the lack of resonance contributions for the $-NMe_3^+$ groups results in the higher A_z for the complex supported by ^{NMe3}L.

With the goal of evaluating how the charged $-SO_3^-$ and $-NMe_3^+$ substituents influence the properties and reactivities of the $[CuOH]^{2+}$ core, the products of the one-electron chemical oxidation of $[K(18\text{-crown-6})]_3[^{SO3}LCuOH]$ (4a) and



Figure 11. (a) Plot of $E_{1/2}$ (V vs Fc⁺/Fc measured in DFB) vs σ_p for $[CuOH]^{2+}/[CuOH]^+$ couples supported by the indicated ligands. The line is a fit to the black data points (slope = +0.26). (b) Plot of the hyperfine splitting constant A_z for the $[CuOH]^+$ complexes supported by the indicated ligands. The line is a fit to the black data points, reproduced from ref 4.

 $[^{\text{NMe3}}\text{LCuOH}]\text{BAr}_{4}^{F}$ (**5a**) were studied. Consistent with the electrochemistry results, $[\text{Fc}]\text{BAr}_{4}^{F}$ oxidized **4a**, but the stronger oxidant $[\text{AcFc}]\text{BAr}_{4}^{F}$ was needed to convert **5a**. The oxidation products $[\text{K}(18\text{-crown-6})]_2[^{\text{SO3}}\text{LCuOH}]$ (**8a**) and $[^{\text{NMe3}}\text{LCuOH}](\text{BAr}_{4}^{F})_2$ (**9a**), respectively, were identified on the basis of the similarity of their intense UV–vis features to the signature ligand aryl- π to Cu $d_{x^2-y^2}$ LMCT features of the $[\text{CuOH}]^{2+}$ complexes supported by $^{\text{pyr}}\text{L}^{2-}$, $^{\text{pip}}\text{L}^{2-}$, and $^{\text{NO2}}\text{L}^{2-}$ defined previously.^{2,4,36} Also consistent with the one-electron oxidation reactions to yield **8a** and **9a** were (a) the results of titration experiments that indicated a 1:1 stoichiometry and (b) their second-order HAT reactions with DHA or CHD to yield anthracene or benzene and the respective $[\text{Cu}(\text{OH}_2)]^{2+}$ complexes, identified for the system supported by $^{\text{NMe3}}\text{L}$ via independent synthesis.

With the aim of understanding the HAT reactivity of the new [CuOH]²⁺ complexes 8a and 9a, the BDE of the O-H bond in the product aqua complexes was evaluated (Table 3). The O-H BDEs for $[K(18\text{-crown-6})]_2[^{SO3}LCu(OH_2)]$ (10a) and $[^{NMe3}LCu(OH_2)](BAr_4^F)_2$ (6a) measured in DFB are slightly higher than in the parent complex $^{\text{pyr}}\text{LCu}(\text{OH}_2)$ (3a) by ~0.8 and 1.5 kcal mol⁻¹, respectively. In addition, for the first time, thermodynamic parameters also were obtained in water, which was enabled by the aqueous solubility of the charged complexes. Thus, values of $pK_{a} \approx 8.0$ for $\lceil ^{\rm MMe3}LCu$ - $(OH_2)](ClO_4)_2$ (**6b**) and $E_{1/2} = 1.03$ V (vs NHE) for the $[^{NMe3}LCuOH](ClO_4)_2$ (**9b**)/ $[^{NMe3}LCuOH]ClO_4$ (**5b**) couple yielded an O–H BDE of ~91 kcal mol⁻¹ for 6. A higher pK_a of 10.1 ± 0.2 for [K(18-crown-6)]₂[^{SO3}LCu(OH₂)] (10a) and a lower $E_{1/2} = 0.75$ V (vs NHE) for the [K(18-crown-6)]₂[^{SO3}LCuOH] (8a)/[K(18-crown-6)]₃[^{SO3}LCuOH] (4a) couple resulted in a lower BDE of ~87 kcal mol⁻¹ for 10a. The close agreement of the BDE values determined in organic and aqueous media and with previous values determined in organic solvent for complexes supported by ^{pyr}L²⁻, ^{pip}L²⁻, and $^{NO2}L^{2-}$ is notable.²⁵ Importantly, the complex with higher $E_{1/2}$ supported by ^{NMe3}L has a BDE larger than that supported by $^{SO3}L^{4-}$, consistent with redox potential slightly overwhelming the compensation of pK_a in determining the BDE (eq 1).⁴

On the basis of the thermodynamics for HAT, we anticipated the HAT rates for the [CuOH]²⁺ core supported by ^{NMe3}L to be greater than those supported by $^{5O3}L^{4-}$. However, the second-order rate constant for the reaction of $[^{NMe3}LCuOH](BAr_{4}^{F})_{2}$ (9a) with DHA (DFB, -25 °C) was ~ 160 times smaller than that of $[K(18-crown-6)]_2[^{SO3}LCuOH]$ (8a) (Table 4). In addition, the rate constant further increased for 8a in the presence of excess [Na(15-crown-5)]OTf, an effect that was found via control experiments to not be correlated with an increase in ionic strength. We posit that the increased interaction of $[Na(15\text{-crown-}5)]^+$ with the anionic $-SO_3^-$ groups, particularly in an aprotic solvent such as DFB, causes it to exist as a "tighter ion pair", which mitigates the electrostatic effects of the anionic $-SO_3^-$ moiety to a greater extent than in the presence of $[K(18-crown-6)]^+$. This effect is also manifested in the change in the reduction potential of the $[CuOH]^{2+}/$ $[CuOH]^+$ couple by ~180 mV, which effectively makes 8a' a stronger oxidant. This intrinsic increase in the oxidation potential might translate into a higher thermodynamic driving force for the HAT reaction, which would cause the observed small increase in the rate of HAT from DHA (and CHD).

Using similar thermodynamic arguments, we expected the rate constant for HAT from DHA by [NMe3LCuOH](BArF4)2 (9a) to be similar or perhaps even greater than that of $[^{NO2}LCuOH]$ (2b), as they have essentially identical ΔBDE_{DHA} values (enthalpic driving force, Table 3), and 9a has a slightly higher $E_{1/2}$ value. Yet, the HAT rate constant for 9a is more than 100 times smaller than for 2b, and it is \sim 20 times smaller than that for the parent system [^{pyr}LCuOH] (2a). The discrepancy is illustrated in a plot of log k vs O-HBDE for the series of [CuOH]²⁺ complexes (Figure 12). We postulate that the slow rate for 9a is due to enhanced steric hindrance by the associated BAr^F₄⁻ counteranions. Consistent with such a steric argument, the rate constant for HAT by 9a from CHD, which is significantly smaller than DHA but with a similar C–H BDE, is enhanced by \sim 10-fold relative to that for DHA. The likely presence of tunneling contributions to the HAT reaction rate complicates the analysis, however, as noted



Figure 12. Plot of log k vs O-H BDE for the series of copper(III) hydroxide complexes studied to date.

by temperature dependencies of kinetic isotope effects and computations in previous work,^{3,4} as well as computational analysis of the present work described separately.³⁰

CONCLUSIONS

In summary, two new copper(II) hydroxide ([CuOH]⁺) complexes have been prepared, bearing charged para-NMe₃⁺ or -SO₃ substituents on the flanking aryl rings of the supporting bis(carboxamide)pyridine ligands. X-ray crystallographic and spectroscopic measurements of the [CuOH]⁺ complexes support similar geometries and electronic environments for their Cu(II) centers, as well as significant cationanion interactions in the secondary coordination sphere of the ^{SO3}L⁴⁻ supported compounds. The spectroscopic similarities, however, contrast with the significant differences in electrochemical behavior, as indicated by distinct $E_{1/2}([CuOH]^{2+}/[CuOH]^{+})$ values for the ^{NMe3}L and ^{SO3}L⁴⁻ supported complexes. The former is oxidized at significantly higher potentials when compared to the latter, by as much as 0.275 V. The differential electronic effects of the cationic and anionic substituents are also manifested in the UV-vis spectra of the derived [CuOH]²⁺ species. Interestingly, the oxidation potential of the $-SO_3^-$ appended complexes is greatly enhanced (by ~0.180 V) when measured in the presence of excess Na(15-crown5)⁺, providing evidence for ion-pairing interactions in solution. Perhaps most surprising is the fact that, despite a nearly equal thermodynamic driving force for the HAT reaction with DHA (i.e., almost identical BDE values for the product O–H bond in the $[Cu(OH_2)]^{2+}$ complexes) and greater oxidizing power, the $[CuOH]^{2+}$ complex supported by ^{NMe3}L reacts more than 150 times slower in these reactions than the complex featuring the ^{SO3}L⁴⁻ ligand. We speculate that this difference is due to steric encumbrance of substrate access by the bulky BAr_{4}^{F} counterions in the complex of ^{NMe3}L.³⁶

The results presented here highlight key differences in the way that distal charged substituents influence the electronic environment of the metal center compared to their neutral counterparts. Specifically, these groups can introduce other secondary counterion interactions that can (1) lead to direct thermodynamic consequences through perturbation of the ligand electron donation/withdrawal and (2) affect kinetic barriers, including by sterically crowding the active site of the reactive [CuOH]²⁺ core. While this work corroborates previous findings that the O-H BDE values of the product aqua complexes are key predictors of HAT reactivity (keeping in mind the caveat that tunneling contributions are implicated), it also shows that the influence of counterions in these systems can be significant and that the effects on the reactivity of the [CuOH]²⁺ core are more nuanced than might be suggested simply by analysis of substituent electron

ASSOCIATED CONTENT

Supporting Information

donating/withdrawing effects.

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01529.

> Full descriptions of materials and methods of syntheses and characterizations of studied compounds, determination of pK_a values, full description of kinetics measurements, preparation of aqueous EPR samples (PDF)

Accession Codes

CCDC 1845452-1845455 and 1845463-1845464 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data request/cif, or by emailing data request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: wbtolman@wustl.edu.

ORCID

Debanian Dhar: 0000-0002-3027-0226 Gereon M. Yee: 0000-0001-7481-2018 William B. Tolman: 0000-0002-2243-6409

Author Contributions

^TThese authors contributed equally to the work.

Notes

The authors declare no competing financial interest.

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