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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[†], William B. Tolman^{*}

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

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^F₄[−] or ClO₄[−]) were prepared, in which SO₃[−] or NMe₃⁺ 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 −SO₃[−] 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(OH₂)]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.

Graphical Abstract

^{*}Corresponding Author: wbtolman@wustl.edu.

[†]These authors contributed equally to the work.

ASSOCIATED CONTENT

Supporting Information

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 p*K*_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 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.

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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 $[\text{CuOH}]^{2+}$ 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 $[\text{CuOH}]^{2+}$ 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 $[\text{CuOH}]^{2+}$ 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 ($[\text{CuOH}_2]^{2+}$) product of HAT, but only partially, such that the complex with the highest $[\text{CuOH}]^{2+/+}$ redox potential exhibits the highest HAT thermodynamic driving force (BDE trend $\text{NO}_2\text{LCu}(\text{OH}_2)$ (**3b**) > $\text{pyrLCu}(\text{OH}_2)$ (**3a**) > $\text{pipLCu}(\text{OH}_2)$ (**3c**)). A similar trend in rates of HAT from dihydroanthracene by the corresponding $[\text{CuOH}]^{2+}$ cores was observed (NO_2LCuOH (**2b**) > pyrLCuOH (**2a**) > pipL-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 ($-\text{NMe}_3^+$) or anionic ($-\text{SO}_3^-$) 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.¹¹

With the aforementioned studies as precedents, we hypothesized that charged ligand substituents could have significant effects on the spectroscopic properties and reactivity of the $[\text{CuOH}]^{2+}$ core. Thus, we targeted new complexes of the proligands $[\text{NMe}_3\text{LH}_2]^{2+}$ and $[\text{SO}_3\text{LH}_2]^{2-}$ (Scheme 1) having $-\text{NMe}_3^+$ and $-\text{SO}_3^-$ 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 $[\text{CuOH}]^+$ unit, and the products of their one-electron oxidation comprising the $[\text{CuOH}]^{2+}$ 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 $[\text{CuOH}]^{2+}$ core.

RESULTS

Synthesis and Characterization of Ligands and Copper(II) Complexes.

The proligands $[\text{SO}_3\text{LH}_2]^{2-}$ and $[\text{NMe}_3\text{LH}_2]^{2+}$, 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 $[\text{SO}_3\text{LH}_2]^{2-}$) in the presence of excess base resulted in the formation of the dicarboxamide products $[(i\text{Pr})_2\text{EtNH}]_2[\text{SO}_3\text{LH}_2]$ and NMe_2LH_2 in gram quantities. Further treatment of NMe_2LH_2 with 2 equiv of MeOTf led to the rapid formation of $[\text{NMe}_3\text{LH}_2][\text{OTf}]_2$. Both ligand salts were characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and elemental analyses (Figures S1–S8). The presence of the triflate anion in $[\text{NMe}_3\text{LH}_2][\text{OTf}]_2$ was confirmed from the $^{13}\text{C}\{^1\text{H}\}$ and ^{19}F NMR spectra (Figures S3 and S4). Also, $[(i\text{Pr})_2\text{EtNH}]_2[\text{SO}_3\text{LH}_2]$ 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 counteranion 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 $[\text{M}][\text{SO}_3\text{LCuOH}]$ (**4a**: $\text{M} = [\text{K}(18\text{-crown-6})]^+$, **4b**: $\text{M} = [\text{K}(\text{crypt-222})]^+$) and $[\text{NMe}_3\text{LCuOH}]\text{X}$ (**5a**: $\text{X} = \text{BAr}_4^-$, **5b**: $\text{X} = \text{ClO}_4^-$) were prepared by treatment of the proligand salts with 1 equiv of $\text{Cu}(\text{OTf})_2$ under aqueous conditions in the presence of excess hydroxide (Scheme 2). In the case of $[\text{K}(18\text{-crown-6})]_3[\text{SO}_3\text{LCuOH}]$ (**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 and X-ray crystallography (see below) support the indicated formulation. Further treatment of a solution of **4a** in 1,2-difluorobenzene (DFB) with 5 equiv of crypt-222, followed by recrystallization by vapor diffusion of Et_2O , yielded

blue crystals of $[\text{K}(\text{crypt-222})]_3[\text{SO}_3\text{LCuOH}]$ (**4b**, 0.105 g, 87.0%). The complex $[\text{NMe}_3\text{LCuOH}]\text{BARF}_4$ (**5a**) was synthesized by the addition of 1 equiv of NaBARF_4 to the initial reaction mixture (proligand, base, $\text{Cu}(\text{OTf})_2$), followed by extraction of the aqueous layer with CH_2Cl_2 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 $[\text{NMe}_3\text{LCuOH}]\text{ClO}_4$ (**5b**) was prepared by slow evaporation of the aqueous reaction mixture in the presence of excess NaClO_4 , giving crystals suitable for X-ray diffraction.

Anticipating that $[\text{Cu}(\text{OH}_2)]^{2+}$ cores would form as products of HAT by the $[\text{CuOH}]^{2+}$ complexes of $\text{NMe}_3\text{L}^{2-}$ and SO_3L^{4-} , we sought to prepare these aqua complexes independently. Success was achieved in the case of the former ligand, with $[\text{NMe}_3\text{LCu}(\text{OH}_2)](\text{ClO}_4)_2$ (**6**, 0.0784 g, 37.0%) isolated from the reaction of $[\text{NMe}_3\text{LH}_2][\text{OTf}]_2$, $\text{Cu}(\text{OTf})_2$, and NaClO_4 in H_2O (a BARF_4^- salt was not accessible). The complex crystallizes as a hydrate, as determined by X-ray crystallography and elemental analysis. Similar attempts to synthesize a $[\text{Cu}(\text{OH}_2)]^{2+}$ complex for SO_3L^{4-} led instead to the isolation of a dimer $[(\text{Et}_4\text{N})_2(\text{SO}_3\text{LCu})]_2$ (**7**, 0.120 g, 56.0%), 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 $[\text{SO}_3\text{LCu}]^{2-}$ unit (see below).

X-ray Crystal Structures.—The X-ray structures of the $[\text{CuOH}]^+$ complexes $[\text{M}]_3[\text{SO}_3\text{LCuOH}]$ (**4a**: $\text{M} = \text{K}(\text{18-crown-6})$, **4b**: $\text{M} = \text{K}(\text{crypt-222})$) and $[\text{NMe}_3\text{LCuOH}]\text{ClO}_4$ (**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 $[\text{Bu}_4\text{N}][\text{py}^+\text{LCuOH}]$ (**1a**), $[\text{Et}_4\text{N}][\text{NO}_2\text{LCuOH}]$ (**1b**), and $[\text{Na}][\text{pip}^+\text{LCuOH}]$ (**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 ($\text{K}\cdots\text{O} \approx 2.8$ 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 SO_3^- functionality. In the case of **4b**, the more effective encapsulation of the K^+ ion by the cryptand results in a structure wherein two of the $[\text{K}(\text{crypt-222})]^+$ counterions do not exhibit any significant secondary interactions (Figure 4, top). Notwithstanding what would be expected to be coordinative saturation by the multidentate cryptand ligand, the third $[\text{K}(\text{crypt-222})]^+$ 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 SO_3^- 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 $[^{NMe_3}LCu(OH_2)]-(ClO_4)_2$ (**6**) is shown in Figure S12. The cationic unit closely resembles that in $[^{NMe_3}LCuOH]ClO_4$ (**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 $[(Et_4N)_2(^{SO_3}LCu)]_2$ (**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–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) cores in $[K(18\text{-crown-}6)]_3[^{SO_3}LCuOH]$ (**4a**), $[^{NMe_3}LCuOH]-BARF_4$ (**5a**), and $[Bu_4N][^{Py^T}LCuOH]$ (**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*- SO_3^- and $-Nme_3^+$ substituents have little effect on the UV–vis and EPR spectroscopic features of $[K(18\text{-crown-}6)]_3[^{SO_3}LCuOH]$ (**4a**) and $[^{NMe_3}LCuOH]BARF_4$ (**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 $[K(18\text{-crown-}6)]_3[^{SO_3}LCuOH]$ (**4a**) and $[^{NMe_3}LCuOH]BARF_4$ (**5a**), respectively. The shown cyclic voltammogram (CV) of the parent complex $[Bu_4N][^{Py^T}LCuOH]$ (**1a**) ($E_{1/2} = -0.076$ V), in combination with the previously reported data for $[Et_4N][^{NO_2}LCuOH]$ (**1b**; $E_{1/2} = 0.124$ V) and $[Bu_4N]-[^{pip}LCuOH]$ (**1c**; $E_{1/2} = -0.260$ V),^{3,4} serve as precedent for assignment of the waves for **4a** and **5a** as analogous $[CuOH]^{2+}/[CuOH]^+$ couples. As expected, the electron-withdrawing properties of the NMe_3^+ substituents in **5a** ($\sigma_p = 0.88$) result in a positively shifted redox potential, slightly larger than that seen for **1b** (NO_2 groups $\sigma_p = 0.78$).²⁰ On the contrary, while the $-SO_3^-$ 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 $[Bu_4N][^{Py^T}LCuOH]$ (**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 solution-state spectroscopic and/or electrochemical properties of **4a** or **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*_{||} 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 S19; 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]–[Py^rLCuOH] (**1a**) and [Et₄N][^{NO₂}LCuOH] (**1b**) (*E*_{1/2} ≈ 200 mV).⁴ We interpret the results to suggest that there is a significant difference between the interactions of the pendant –SO₃[–] groups in **4a/4b** with the K⁺-containing counterions compared to [Na(15-crown-5)]⁺. While this difference causes significant changes in the redox potential, the UV–vis and EPR 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 –SO₃[–] 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 –SO₃[–] 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-crown-6)]₃[^{SO₃}LCuOH] (**4a**) and [^{NMe₃}LCuOH]BAR^F₄ (**5a**) in DFB with 1 equiv of oxidant ([Fc]BAR^F₄ for **4a**; [AcFc]BAR^F₄ 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 results of previous studies, we attribute these features to ligand aryl π to Cu d_{x²–y²} 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 -NMe⁺ 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[^{SO}₃LCuOH] (**4a**) also was found to be sensitive to the nature of the counteranion. In the presence of [Na(15-crown-5)]OTf (100 equiv), the reaction of **4a** with [Fc]BARF₄ did not proceed to give **8a** as shown above. Conversion to **8a'** instead required the use of the stronger oxidant [AcFc]BARF₄ ($E_{1/2} \approx 0.27$ 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]BARF₄) 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-crown-6)]₂[^{SO}₃LCuOH] (**8a**, M = Na or K) relative to those of [NMe₃LCuOH](BARF₄)₂ (**9a**) also are consistent with the expected effects on the ligand-centered HOMO (more electron-withdrawing –Nme₃⁺ substituent increases energy of ligand $\pi \rightarrow \text{Cu } d_{x^2-y^2}$ 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(OH₂)]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⁺ complex were inserted into eq 1 (where C_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 [Cu(OH₂)]²⁺ complex of another (L') and measuring the K_{eq} for the resulting equilibrium expressed by Scheme 4. The difference in the BDE values (BDE) between the two [Cu(OH₂)]²⁺ cores may then be approximated by $-RT\ln K_{eq}$, under the assumption that S_{rxn} is negligible and H_{rxn} is independent of temperature. We considered

both methods in seeking to determine the BDE values for the $[\text{Cu}(\text{OH}_2)]^{2+}$ cores supported by $^{\text{NMe}_3}\text{L}$ and $^{\text{SO}_3}\text{L}^{4-}$ and to compare them to the values previously determined for **3a–c**.

$$\text{BDE} \left(\text{kcal mol}^{-1} \right) = 1.37 \text{ p}K_{\text{a}} + 23.06 E^{\circ} + C_{\text{H}} \quad (1)$$

Thus, $[\text{K}(\text{18-crown-6})]_2[^{\text{SO}_3}\text{LCuOH}]$ (**8a**) was generated by reaction of $[\text{K}(\text{18-crown-6})]_3[^{\text{SO}_3}\text{LCuOH}]$ (**4a**) with $[\text{Fc}]\text{BARF}_4$ (1 equiv) in DFB at -25°C and then treated with varying amounts of the parent aqua complex $^{\text{pyr}}\text{LCu}-(\text{OH}_2)$ (**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 $^{\text{pyr}}\text{LCuOH}$ (**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 $K_{\text{eq}} = 4.2 \pm 1.8$ (illustrative deconvolution traces shown in Figure S25), corresponding to a BDE of $\sim 0.8 \text{ kcal mol}^{-1}$, such that the O–H BDE for $[\text{K}(\text{18-crown-6})]_2[^{\text{SO}_3}\text{LCu}(\text{OH}_2)]$ (**10a**) is $\sim 0.8 \text{ kcal mol}^{-1}$ stronger than that for **3a** ($90 \pm 3 \text{ kcal mol}^{-1}$; Table 3).³

Unfortunately, the cross-HAT protocol proved unsuitable for determining the O–H BDE of $[\text{NMe}_3\text{LCu}(\text{OH}_2)](\text{BARF}_4)_2$ (**6a**), the product of HAT by $[\text{NMe}_3\text{LCuOH}](\text{BARF}_4)_2$ (**9a**), owing to difficulties in reproducibly determining the point of equilibrium. However, addition of an excess of $[\text{pyr}]\text{LCu}(\text{OH}_2)$ (**3a**, 2.5 equiv) to a solution of **9a** (generated by oxidation of **5a** with 1 equiv of $[\text{AcFc}]\text{BARF}_4$ in DFB solvent at -25°C) resulted in the complete conversion of **3a** to $^{\text{pyr}}\text{LCuOH}$ (**2a**) within $\sim 2 \text{ min}$ (Figure S26). Assuming $\sim 95\%$ conversion of **3a** of **2a**, we estimate the K_{eq} for this reaction to be ~ 11 , which gives a BDE between **3a** and **6a** of $\sim 1.5 \text{ kcal mol}^{-1}$, 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 $\sim 91.5 \text{ kcal mol}^{-1}$ (Table 3).

To further validate the results from the cross-HAT experiments, we took advantage of the water solubility of $[\text{K}(\text{18-crown-6})]_3[^{\text{SO}_3}\text{LCuOH}]$ (**4a**) and $[\text{NMe}_3\text{LCuOH}]\text{ClO}_4$ (**5b**) to more directly evaluate the BDE of the O–H bonds in $[\text{K}(\text{18-crown-6})]_2[^{\text{SO}_3}\text{LCu}(\text{OH}_2)]$ (**10a**) and $[\text{NMe}_3\text{LCu}-(\text{OH}_2)](\text{ClO}_4)_2$ (**6b**) using eq 1, where $C_{\text{H}} = 55.8 \text{ kcal mol}^{-1}$.²⁵ The $\text{p}K_{\text{a}}$ 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 HClO_4 and measured using a pH probe (Figure S27, 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 $\text{p}K_{\text{a}}$ 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 $\text{p}K_{\text{a}}$ of $[\text{NMe}_3\text{LCu}(\text{OH}_2)](\text{ClO}_4)_2$ (**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 $\text{p}K_{\text{a}}$ 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 one-electron 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(OH₂)]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-crown-6)]₂[^{SO3}LCuOH] (**8a**) and [^{NMe3}LCuOH](BAR^F₄) (**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-crown-6)]₂[^{SO3}LCuOH] (**8a**) to react most rapidly with DHA, with a rate constant similar to that measured for **2b** supported by NO₂L²⁻ 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^F₄)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^F₄⁻ 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 ± 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 ($70(8) \text{ M}^{-1} \text{ s}^{-1}$; 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 $[\text{CuOH}]^{2+}/[\text{CuOH}]^+$ 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 $[\text{Na}(15\text{-crown-5})]\text{OTf}$ and yielded a slightly larger second-order rate constant (k) of $500(30) \text{ M}^{-1} \text{ s}^{-1}$ (Figure 10, Table 4). Concerned that changes in the ionic strength might affect the reaction rate,³³ we performed a control reaction of **8a** with DHA in the presence of 100 equiv of $[\text{Bu}_4\text{N}]\text{PF}_6$ (Figure 10). The observed rate constant in this case was found to be $300(12) \text{ M}^{-1} \text{ s}^{-1}$, 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 $[\text{Bu}_4\text{N}]\text{BAR}^{\text{F}}$ yielded no difference in the rate of HAT. Taken together, these data provide firm evidence for an intrinsic difference in the influence of the $[\text{Na}(15\text{-crown-5})]^+$ and $[\text{K}(18\text{-crown-6})]^+$ counterions on the HAT properties of the $[\text{CuOH}]^{2+}$ 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 $-\text{SO}_3^-$ or $-\text{Nme}_3^+$ substituents, we prepared and characterized the Cu(II) hydroxide ($[\text{CuOH}]^+$) complexes $[\text{M}]_3[\text{SO}_3\text{LCuOH}]$ (**4a**: $\text{M} = [\text{K}(18\text{-crown-6})]^+$, **4b**: $\text{M} = [\text{K}(\text{crypt-222})]^+$) and $[\text{NMe}_3\text{LCuOH}]\text{X}$ (**5a**: $\text{X} = \text{BAR}_4^{\text{F}-}$, **5b**: $\text{X} = \text{ClO}_4^-$). A key question we wished to address was how the charged substituents influenced the properties of the $[\text{CuOH}]^+$ 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 $-\text{SO}_3^-$ 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 $-\text{SO}_3^-$ units to act as ligands was further illustrated in the X-ray structure of $[(\text{Et}_4\text{N})_2(\text{SO}_3\text{LCu})]_2$ (**7**), which was isolated in attempts to prepare a $[\text{Cu}(\text{OH}_2)]^{2+}$ complex. UV–Vis and EPR spectra of the $[\text{CuOH}]^+$ 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 $[\text{CuOH}]^{2+}/[\text{CuOH}]^+$ couples were observed, which varied as a function of the supporting ligand substituents and, for the $-\text{SO}_3^-$ system, the nature of the counteranion (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 pyrL^{2-} , NO_2L^{2-} , and NMe_3L ligands, but those featuring the SO_3L^{2-} ligand with either K^+ or Na^+ counterions fall off the line (Figure 11a). We attribute this observation to the use of a single σ_p value for the $-\text{SO}_3^-$ group (reported from measurements in water)²⁰ that does not take into consideration the effects of interactions with counteranions 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 $-\text{SO}_3^-$ 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 pipL^{2-} , pyrL^{2-} , and NO_2L^{2-} (black circles). The data for the new ligands with $-\text{Nme}_3^+$ and $-\text{SO}_3^-$ substituents do not fit to this line, however. As noted above, the disparity for the SO_3L^{4-} systems with Na^+ and K^+ counteranions is likely due to ionic interactions that modulate the electron-withdrawing properties of the $-\text{SO}_3^-$ moiety. A different explanation is needed to rationalize the significant difference in A_z values for the NMe_3L system compared to that comprising NO_2L^{2-} that has similarly electron-withdrawing $-\text{NO}_2$ groups (with a similar σ_p value). We postulate different sensitivity of A_z to resonance and field effects that contribute to σ_p , as it is known that the $-\text{NO}_2$ and $-\text{NMe}_3^+$ 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 $-\text{Nme}_3^+$ groups results in the higher A_z for the complex supported by NMe_3L .

With the goal of evaluating how the charged $-\text{SO}_3^-$ and $-\text{Nme}_3^+$ substituents influence the properties and reactivities of the $[\text{CuOH}]^{2+}$ core, the products of the one-electron chemical oxidation of $[\text{K}(\text{18-crown-6})]_3[\text{SO}_3\text{LCuOH}]$ (**4a**) and $[\text{NMe}_3\text{LCuOH}]\text{BAR}_4^{\text{F}}$ (**5a**) were studied. Consistent with the electrochemistry results, $[\text{Fc}]\text{BAR}_4^{\text{F}}$ oxidized **4a**, but the stronger oxidant $[\text{AcFc}]\text{BAR}_4^{\text{F}}$ was needed to convert **5a**. The oxidation products $[\text{K}(\text{18-crown-6})]_2[\text{SO}_3\text{LCuOH}]$ (**8a**) and $[\text{NMe}_3\text{LCuOH}](\text{BAR}_4^{\text{F}})_2$ (**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 pyrL^{2-} , pipL^{2-} , and NO_2L^{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 NMe_3L via independent synthesis.

With the aim of understanding the HAT reactivity of the new $[\text{CuOH}]^{2+}$ 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 $[\text{K}(\text{18-crown-6})]_2[\text{SO}_3\text{LCu}(\text{OH}_2)]$ (**10a**) and $[\text{NMe}_3\text{LCu}(\text{OH}_2)](\text{BAR}_4^{\text{F}})_2$ (**6a**) measured in DFB are slightly higher than in the parent complex $\text{pyrLCu}(\text{OH}_2)$ (**3a**) by ~ 0.8 and $1.5 \text{ kcal mol}^{-1}$, 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 $\text{p}K_a \approx 8.0$ for $[\text{NMe}_3\text{LCu}(\text{OH}_2)](\text{ClO}_4)_2$ (**6b**) and $E_{1/2} = 1.03 \text{ V}$

(vs NHE) for the $[\text{NMe}_3\text{LCuOH}](\text{ClO}_4)_2$ (**9b**)/ $[\text{NMe}_3\text{LCuOH}]\text{ClO}_4$ (**5b**) couple yielded an O–H BDE of $\sim 91 \text{ kcal mol}^{-1}$ for **6**. A higher $\text{p}K_a$ of 10.1 ± 0.2 for $[\text{K}(18\text{-crown-6})]_2[\text{SO}_3\text{LCu}(\text{OH}_2)]$ (**10a**) and a lower $E_{1/2} = 0.75 \text{ V}$ (vs NHE) for the $[\text{K}(18\text{-crown-6})]_2[\text{SO}_3\text{LCuOH}]$ (**8a**)/ $[\text{K}(18\text{-crown-6})]_3[\text{SO}_3\text{LCuOH}]$ (**4a**) couple resulted in a lower BDE of $\sim 87 \text{ kcal mol}^{-1}$ 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 pyrL^{2-} , pipL^{2-} , and NO_2L^{2-} is notable.²⁵ Importantly, the complex with higher $E_{1/2}$ supported by NMe_3L has a BDE larger than that supported by SO_3L^{4-} , consistent with redox potential slightly overwhelming the compensation of $\text{p}K_a$ in determining the BDE (eq 1).⁴

On the basis of the thermodynamics for HAT, we anticipated the HAT rates for the $[\text{CuOH}]^{2+}$ core supported by NMe_3L to be greater than those supported by SO_3L^{4-} . However, the second-order rate constant for the reaction of $[\text{NMe}_3\text{LCuOH}](\text{BAR}^{\text{F}}_4)_2$ (**9a**) with DHA (DFB, -25°C) was ~ 160 times *smaller* than that of $[\text{K}(18\text{-crown-6})]_2[\text{SO}_3\text{LCuOH}]$ (**8a**) (Table 4). In addition, the rate constant further increased for **8a** in the presence of excess $[\text{Na}(15\text{-crown-5})]\text{OTf}$, 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 $[\text{Na}(15\text{-crown-5})]^+$ with the anionic $-\text{SO}_3^-$ 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 $-\text{SO}_3^-$ moiety to a greater extent than in the presence of $[\text{K}(18\text{-crown-6})]^+$. This effect is also manifested in the change in the reduction potential of the $[\text{CuOH}]^{2+}/[\text{CuOH}]^+$ couple by $\sim 180 \text{ mV}$, 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 $[\text{NMe}_3\text{LCuOH}](\text{BAR}^{\text{F}}_4)_2$ (**9a**) to be similar or perhaps even greater than that of $[\text{NO}_2\text{LCuOH}]$ (**2b**), as they have essentially identical BDE_{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 ~ 20 times smaller than that for the parent system $[\text{pyrL}]\text{CuOH}$ (**2a**). The discrepancy is illustrated in a plot of $\log k$ vs O–H BDE for the series of $[\text{CuOH}]^{2+}$ complexes (Figure 12). We postulate that the slow rate for **9a** is due to enhanced steric hindrance by the associated $\text{BAR}^{\text{F}}_4^-$ 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 ~ 10 -fold relative to that for DHA. The likely presence of tunneling contributions to the HAT reaction rate complicates the analysis, however, as noted 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.³⁶

CONCLUSIONS

In summary, two new copper(II) hydroxide ($[\text{CuOH}]^+$) complexes have been prepared, bearing charged *para*- NMe_3^+ or $-\text{SO}_3^-$ substituents on the flanking aryl rings of the

supporting bis(carboxamide)pyridine ligands. X-ray crystallographic and spectroscopic measurements of the $[\text{CuOH}]^+$ complexes support similar geometries and electronic environments for their Cu(II) centers, as well as significant cation–anion interactions in the secondary coordination sphere of the SO_3L^{4-} supported compounds. The spectroscopic similarities, however, contrast with the significant differences in electrochemical behavior, as indicated by distinct $E_{1/2}([\text{CuOH}]^{2+}/[\text{CuOH}]^+)$ values for the NMe_3L and SO_3L^{4-} 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 $[\text{CuOH}]^{2+}$ species. Interestingly, the oxidation potential of the $-\text{SO}_3^-$ appended complexes is greatly enhanced (by ~ 0.180 V) when measured in the presence of excess $\text{Na}(15\text{-crown5})^+$, 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 $[\text{Cu}(\text{OH}_2)]^{2+}$ complexes) and greater oxidizing power, the $[\text{CuOH}]^{2+}$ complex supported by NMe_3L reacts more than 150 times *slower* in these reactions than the complex featuring the SO_3L^{4-} 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 NMe_3L .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 $[\text{CuOH}]^{2+}$ 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 $[\text{CuOH}]^{2+}$ core are more nuanced than might be suggested simply by analysis of substituent electron donating/withdrawing effects.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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REFERENCES

- (1). (a) Solomon EI; Heppner DE; Johnston EM; Ginsbach JW; Cirera J; Qayyum M; Kieber-Emmons MT; Kjaergaard CH; Hadt RG; Tian L Copper Active Sites in Biology. *Chem. Rev* 2014, 114, 3659–3853. [PubMed: 24588098] (b) Mirica LM; Ottenwaelter X; Stack TDP Structure and Spectroscopy of Copper–Dioxygen Complexes. *Chem. Rev* 2004, 104, 1013–1045. [PubMed:

- 14871148] (c)Lewis EA; Tolman WB Reactivity of Dioxygen–Copper Systems. *Chem. Rev* 2004, 104, 1047–1076. [PubMed: 14871149] (d)Elwell CE; Gagnon NL; Neisen BD; Dhar D; Spaeth AD; Yee GM; Tolman WB Copper–Oxygen Complexes Revisited: Structures, Spectroscopy, and Reactivity. *Chem. Rev* 2017, 117, 2059–2107. [PubMed: 28103018] (e)Allen SE; Walvoord RR; Padilla-Salinas R; Kozlowski MC Aerobic Copper-Catalyzed Organic Reactions. *Chem. Rev* 2013, 113, 6234–6458. [PubMed: 23786461] (f)Serrano-Plana J; Garcia-Bosch I; Company A; Costas M Structural and Reactivity Models for Copper Oxygenases: Cooperative Effects and Novel Reactivities. *Acc. Chem. Res* 2015, 48, 2397–2406. [PubMed: 26207342] (g)Copper-Oxygen Chemistry; Karlin KD, Itoh S, Rokita S, Eds.; Wiley Series of Reactive Intermediates in Chemistry and Biology; John Wiley & Sons, Inc.: Hoboken, NJ, 2011; Vol. 4.
- (2). Donoghue PJ; Tehranchi J; Cramer CJ; Sarangi R; Solomon EI; Tolman WB Rapid C–H Bond Activation by a Monocopper(III)–Hydroxide Complex. *J. Am. Chem. Soc* 2011, 133, 17602–17605. [PubMed: 22004091]
 - (3). Dhar D; Tolman WB Hydrogen Atom Abstraction from Hydrocarbons by a Copper(III)-Hydroxide Complex. *J. Am. Chem. Soc* 2015, 137, 1322–1329. [PubMed: 25581555]
 - (4). Dhar D; Yee GM; Spaeth AD; Boyce DW; Zhang H; Dereli B; Cramer CJ; Tolman WB Perturbing the Copper(III)-Hydroxide Unit through Ligand Structural Variation. *J. Am. Chem. Soc* 2016, 138, 356–368. [PubMed: 26693733]
 - (5). Dhar D; Yee GM; Markle TF; Mayer JM; Tolman WB Reactivity of the Copper(III)-Hydroxide Unit with Phenols. *Chem. Sci* 2017, 8, 1075–1085. [PubMed: 28572905]
 - (6). (a)Frandsen KEH; Simmons TJ; Dupree P; Poulsen J-CN; Hemsworth GR; Ciano L; Johnston EM; Tovborg M; Johansen KS; von Freiesleben P; Marmuse L; Fort S; Cottaz S; Driguez H; Henrissat B; Lenfant N; Tuna F; Baldansuren A; Davies GJ; Lo Leggio L; Walton PH The molecular basis of polysaccharide cleavage by lytic polysaccharide monooxygenases. *Nat. Chem. Biol* 2016, 12, 298–303. [PubMed: 26928935] (b)Quist DA; Diaz DE; Liu JJ; Karlin KD Activation of dioxygen by copper metalloproteins and insights from model complexes. *JBIC, J. Biol. Inorg. Chem* 2017, 22, 253–288. [PubMed: 27921179] (c)Hedegård ED; Ryde U Targeting the reactive intermediate in polysaccharide monooxygenases. *JBIC, J. Biol. Inorg. Chem* 2017, 22, 1029–1037. [PubMed: 28698982]
 - (7). (a)Shook RL; Borovik AS Role of the secondary coordination sphere in metal-mediated dioxygen activation. *Inorg. Chem* 2010, 49, 3646–3660. [PubMed: 20380466] (b)Cook SA; Borovik AS Molecular designs for controlling the local environments around metal ions. *Acc. Chem. Res* 2015, 48, 2407–2414. [PubMed: 26181849] (c)Mann SI; Heinisch T; Ward TR; Borovik AS Peroxide activation regulated by hydrogen bonds within artificial Cu proteins. *J. Am. Chem. Soc* 2017, 139, 17289–17292. [PubMed: 29117678] (d)Creutz SE; Peters JC Exploring secondary-sphere interactions in Fe–N_xH_y complexes relevant to N₂ fixation. *Chem. Sci* 2017, 8, 2321–2328. [PubMed: 28451336]
 - (8). (a)Wang D; Groves JT Efficient water oxidation catalyzed by homogeneous cationic cobalt porphyrins with critical roles for the buffer base. *Proc. Natl. Acad. Sci. U. S. A* 2013, 110, 15579–15584. [PubMed: 24019473] (b)Bell SR; Groves JT A Highly Reactive P450 Model Compound I. *J. Am. Chem. Soc* 2009, 131, 9640–9641. [PubMed: 19552441] (c)Gao H; Groves JT Fast Hydrogen Atom Abstraction by a Hydroxo Iron(III) Porphyrine. *J. Am. Chem. Soc* 2017, 139, 3938–3941. [PubMed: 28245648]
 - (9). Nakano K; Kamada T; Nozaki K Selective formation of polycarbonate over cyclic carbonate: Copolymerization of epoxides with carbon dioxide catalyzed by a cobalt(III) complex with a piperidinium end-capping arm. *Angew. Chem., Int. Ed* 2006, 45, 7274–7277.
 - (10). Boaz NC; Bell SR; Groves JT Ferryl Protonation in Oxoiron(IV) Porphyrins and Its Role in Oxygen Transfer. *J. Am. Chem. Soc* 2015, 137, 2875–2885. [PubMed: 25651467]
 - (11). (a)Yoshida M; Kondo M; Torii S; Sakai K; Masaoka S Oxygen Evolution Catalyzed by a Mononuclear Ruthenium Complex Bearing Pendant SO₃[–] Groups. *Angew. Chem., Int. Ed* 2015, 54, 7981–7984. (b)Hardouin Duparc V; Schaper F Sulfonato-imino copper(II) complexes: fast and general Chan–Evans–Lam coupling of amines and anilines. *Dalton Trans* 2017, 46, 12766–12770. [PubMed: 28920613] (c)Hardouin Duparc V; Schaper F Sulfonato-diketimine Copper-(II) Complexes: Synthesis and Application as Catalysts in Chan–Evans–Lam Couplings. *Organometallics* 2017, 36, 3053–3060.

- (12). Taylor R; Kennard O; Versichel W Geometry of the N-H-O = C Hydrogen Bond. 2. Three-Center ("Bifurcated") and Four-Center ("Trifurcated") Bonds. *J. Am. Chem. Soc* 1984, 106, 244–248.
- (13). Yang L; Powell DR; Houser RP Structural variation in copper(I) complexes with pyridylmethanamide ligands: structural analysis with a new four-coordinate geometry index, τ_4 . *Dalton Transactions* 2007, 9, 955–964.
- (14). Spaeth AD; Gagnon NL; Dhar D; Yee GM; Tolman WB Determination of the Cu(III)-OH Bond Distance by Resonance Raman Spectroscopy Using a Normalized Version of Badger's Rule. *J. Am. Chem. Soc* 2017, 139, 4477–4485. [PubMed: 28319386]
- (15). This ionic interaction between the SO_3^- group and the $[\text{K}(18\text{-C-}6)]^+$ is accompanied by severe positional disorder in the X-ray structure, which results from the rotation of the SO_3^- group that is coupled with rotational disorder in the crown moieties. As a result, both the SO_3^- groups and the coupled $[\text{K}(18\text{-C-}6)]^+$ fragments needed to be modeled using a two-part disorder component.
- (16). Murata M; Kojima M; Kita M; Kashino S; Yoshikawa Y A Stable Su Ifonato-Cobalt(III) Complex: $[\text{Co}\{\text{OS}(\text{O})_2\text{CH}_2\text{CH}_2\text{NH}_2\text{-N,O}\}(\text{en})_2](\text{ClO}_4)_2$. *Acta Crystallogr* 1997, C53, 1761–1762.
- (17). The UV–vis and EPR spectra for 4a and 4b are identical (Figure S13).
- (18). (a)Bales BL; Peric M EPR Line Shifts and Line Shape Changes Due to Spin Exchange of Nitroxide Free Radicals in Liquids. *J. Phys. Chem. B* 1997, 101, 8707–8716.(b)Bales BL; Meyer M; Smith S; Peric M EPR Line Shifts and Line Shape Changes due to Spin Exchange of Nitroxide Free Radicals in Liquids: 6. Separating Line Broadening due to Spin Exchange and Dipolar Interactions. *J. Phys. Chem. A* 2009, 113, 4930–4940. [PubMed: 19385676]
- (19). O'Toole TR; Younathan JN; Sullivan BP; Meyer TJ 1,2-Difluorobenzene: a relatively inert and noncoordinating solvent for electrochemical studies on transition-metal complexes. *Inorg. Chem* 1989, 28, 3923–3926.
- (20). (a)Values from Issacs, N. *Physical Organic Chemistry*, 2nd ed.; Longman Scientific & Technical: London, U.K., 1995; pp 152–153, which lists averaged values reported in Exner, O. in *Correlation Analysis in Chemistry*, Chapman, N. B. and Shorter, J., Eds.; Longman Scientific & Technical Plenum: London, U.K., 1978; Chapter 10.(b)Slightly different values of $\sigma_p = 0.82$ (NMe_3^+) and a significantly different value of $\sigma_p = 0.35$ (SO_3^-) Hansch C; Leo A; Taft RW *Chem. Rev* 1991, 91, 165–195.
- (21). As expected in the presence of excess Bu_4NPF_6 electrolyte, the CV of 4b in DFB solvent exhibits an essentially identical $E_{1/2}$ of -0.140 V versus Fc^+/Fc , albeit with reduced cathodic reversibility (Figure S18). We speculate that the reduced cathodic reversibility is due to reaction of the generated $[\text{CuOH}]_2^+$ core with C–H bonds in the cryptand.
- (22). Chang KB; Vinokur A; Pinlac RAF; Suchomel MR; Marvel MR; Poeppelmeier KR How lewis acidity of the cationic framework affects KNaNbOF_5 polymorphism. *Inorg. Chem* 2014, 53, 6979–6984. [PubMed: 24922362]
- (23). Attempted oxidation of 4b with $[\text{Fc}][\text{BArF}_4]$ at -25°C produced similar charge transfer features as 8a, but this species is highly unstable and decays almost instantaneously. This is in agreement with the reduced cathodic reversibility observed previously in the cyclic voltammetry experiments.
- (24). Connelly NG; Geiger WE Chemical Redox Agents for Organometallic Chemistry. *Chem. Rev* 1996, 96, 877–910. [PubMed: 11848774]
- (25). Warren JJ; Tronic TA; Mayer JM Thermochemistry of Proton-Coupled Electron Transfer Reagents and its Implications. *Chem. Rev* 2010, 110, 6961–7001. [PubMed: 20925411]
- (26). We hypothesize that the $-\text{SO}_3^-$ group remains deprotonated in this pH range and that all the protonation/deprotonation events occur on the Cu(II)-bound hydroxide/aqua moiety. Attempts to reduce the pH of the solution below 4 results in significant bleaching of the UV–vis absorption features, possibly due to protonation of the pendant $-\text{SO}_3^-$. This observation is in congruence with the reported pK_a of 3.25 for 4-aminobenzenesulfonic acid (vide Skripnikova TA; Lysova SS; Zevatskii YE Determination of the dissociation constants of 5-substituted 1*H*-tetrazoles and amino acids by the concentration spectrophotometric method: A new approach. *J. Chem. Eng. Data* 2017, 62, 2400–2405.

- (27). Dissolution of $(\text{Et}_4\text{N})_2(\text{SO}_3\text{LCu})_2$ (7) in water results in identical spectra at the corresponding pH values, which is consistent with the notion that the dimeric unit forms the corresponding $[\text{Cu}(\text{OH}_2)_2]^{2+}$ when dissolved in water.
- (28). (a) Shen J; Wang M; Zhang P; Jiang J; Sun L Electrocatalytic water oxidation by copper(II) complexes containing a tetra- or pentadentate amine-pyridine ligand. *Chem. Commun* 2017, 53, 4374–4377. (b) Garrido-Barros P; Funes-Ardoiz I; Drouet S; Benet-Buchholz J; Maseras F; Llobet A Redox Non-innocent Ligand Controls Water Oxidation Overpotential in a New Family of Mononuclear Cu-Based Efficient Catalysts. *J. Am. Chem. Soc* 2015, 137, 6758–6761. [PubMed: 25984748] (c) Yu F; Li F; Hu J; Bai L; Zhu Y; Sun L Electrocatalytic water oxidation by a macrocyclic Cu(II) complex in neutral phosphate buffer. *Chem. Commun* 2016, 52, 10377–10380. (d) Fu L-Z; Fang T; Zhou L-L; Zhan S-Z A mononuclear copper electrocatalyst for both water reduction and oxidation. *RSC Adv* 2014, 4, 53674–53680. (e) Coggins MK; Zhang M-T; Chen Z; Song N; Meyer TJ Single-Site Copper(II) Water Oxidation Electrocatalysis: Rate Enhancements with HPO_4^{2-} as a Proton Acceptor at pH 8. *Angew. Chem., Int. Ed* 2014, 53, 12226–12230.
- (29). It is worth noting that, despite the agreement between the two estimated BDE values, these are measured in different solvents. It is well-documented in literature that BDE values are somewhat solvent-dependent, and we anticipate that this is true in our case too. Hence, we choose to roughly approximate an error of $\sim 3 \text{ kcal mol}^{-1}$ on this BDE estimate. As, for example, for a series of phenols, the BDE values in water versus benzene differ by $\sim 1\text{--}3 \text{ kcal mol}^{-1}$ with the BDE values in water being lower than in hydrophobic solvents. (See ref 25 for details.)
- (30). Luo Y-R Comprehensive Handbook of Chemical Bond Energies; CRC Press, Taylor & Francis Group: Boca Raton, FL, 2007.
- (31). Klein JEMN; Dereli B; Que L; Cramer CJ Why metaloxos react with dihydroanthracene and cyclohexadiene at comparable rates, despite having different C-H bond strengths. A computational study. *Chem. Commun* 2016, 52, 10509–10512.
- (32). (a) England J; Martinho M; Farquhar ER; Frisch JR; Bominaar EL; Münck E; Que L A synthetic high-spin oxoiron(IV) complex: generation, spectroscopic characterization, and reactivity. *Angew. Chem., Int. Ed* 2009, 48, 3622–3626. (b) Herres-Pawlis S; Verma P; Haase R; Kang P; Lyons CT; Wasinger EC; Floerke U; Henkel G; Stack TDP Phenolate hydroxylation in a Bis(μ -oxo)dicopper(III) complex: Lessons from the Guanidine/amine series. *J. Am. Chem. Soc* 2009, 131, 1154–1169. [PubMed: 19119846]
- (33). Warren JJ; Mayer JM Tuning the thermochemical and kinetic properties of ascorbate by its local environment: Solution chemistry and biochemical implications. *J. Am. Chem. Soc* 2010, 132, 7784–7793. [PubMed: 20476757]
- (34). We also performed the corresponding experiment in the presence of 100 equiv of $[(\text{K}(18\text{-crown-6)})\text{OTf}]$. This second-order rate constant also had the same value of $300(30) \text{ M}^{-1} \text{ s}^{-1}$, indicating that the rate alteration caused due to change in the ionic strength of the medium is independent of the nature of the added electrolyte.
- (35). Hansch C; Leo A; Taft RW A survey of Hammett substituent constants and resonance and field parameters. *Chem. Rev* 1991, 91, 165–195.
- (36). Additional insights are provided in the computational study accompanying this paper: Dereli B; Momeni MR; Cramer CJ Density Functional Modeling of Ligand Effects on Electronic Structure and C–H Bond Activation Activity of Copper(III) Hydroxide Compounds. *Inorg. Chem* 2018, DOI: 10.1021/ic8b01530.

Figure 1.

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

Figure 2.

Depictions of the X-ray crystal structures of the anionic portion of $[\text{K}(\text{18-crown-6})]_3[\text{SO}_3\text{LCuOH}]$ (**4a**, top) and cationic portion of $[\text{NMe}_3\text{LCuOH}]\text{ClO}_4$ (**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).

Figure 3.

Additional views of the X-ray crystal structure of [K(18-crown-6)]₃[SO₃LCuOH] (**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 $[K(\text{crypt-222})]_3[\text{SO}_3\text{LCuOH}]$ (**4b**), showing the anionic portion and the $[K(\text{crypt-222})]^+$ 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%).

Figure 5.

Depiction of the anionic portion of the X-ray crystal structure of $[(Et_4N)_2(SO_3LCu)]_2$ (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).

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.

Figure 7. CVs of $[\text{K}(18\text{-crown-6})]_3[\text{SO}_3\text{LCuOH}]$ (**4a**) (blue), $[\text{NMe}_3\text{LCuOH}]\text{BAr}^{\text{F}}_4$ (**5a**) (red), and $[\text{Bu}_4\text{N}][\text{Py}^+\text{LCuOH}]$ (**1a**) (black dotted). Conditions: 2 mM analyte in DFB solvent, 0.2 M Bu_4NPF_6 (0.2 M $\text{Bu}_4\text{NBAr}^{\text{F}}_4$ in case of **5a**; data for this electrolyte provided in Figures S9 and S10).

Figure 8.

(top) Overlay of EPR spectra of $[\text{K}(\text{18-crown-6})]_3[\text{SO}_3\text{LCuOH}]$ (**4a**) both in the absence (black) and presence (blue) of 100 equiv of $[\text{Na}(\text{15-crown-5})]\text{OTf}$. 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 $[\text{Na}(\text{15-crown-5})]\text{OTf}$. Conditions: 2 mM analyte in DFB solvent, 0.2 M Bu_4NPF_6 , 50 mV/s.

Figure 9. Overlay of UV-vis spectra. Red (solid line): $[\text{K}(\text{18-crown-6})]_2[\text{SO}_3\text{LCuOH}]$ (**8a**); blue: $[\text{NMe}_3\text{LCuOH}](\text{BAR}^{\text{F}}_4)_2$ (**9a**); black (dotted): NO_2LCuOH (**2b**); red (dashed): $[\text{K}(\text{18-crown-6})]_2[\text{SO}_3\text{LCuOH}] + 100 \text{ equiv of } [\text{Na}(\text{15-crown-5})]\text{OTf}$ (**8a'**).

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 $\text{Bu}_4\text{NBAr}^{\text{F}}$ in DFB at -25°C .

Figure 11.

(a) Plot of $E_{1/2}$ (V vs Fc^+/Fc measured in DFB) vs σ_p for $[\text{CuOH}]^{2+}/[\text{CuOH}]^+$ 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 $[\text{CuOH}]^+$ complexes supported by the indicated ligands. The line is a fit to the black data points, reproduced from ref 4.

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

Scheme 1.

Synthesis of Proligand Salts $[(iPr)_2EtNH][SO_3LH_2]$ (top) and $[NMe_3LH_2][OTf]_2$ (bottom)

Scheme 2.

Synthesis of Copper(II) Hydroxide Precursor Complexes

Scheme 3.

Oxidation Reactions of 4a to 8a and 5a to 9a

Scheme 4.

Equilibrium Measured to Determine the BDE between $[\text{Cu}(\text{OH}_2)]^{2+}$ Cores

Table 1.Comparison of Selected Interatomic Distances (Å) for [CuOH]⁺ Complexes^a

compound	Cu1–OH	Cu1–N2	Cu1–N1/N3	τ_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
[^{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), 2.019(3)	0.16
Et ₄ N][^{NO2} LCuOH] (1b) ^c	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

^aEstimated standard deviations are indicated in parentheses.^bReference 14.^cFrom ref 4.^dTwo molecules in the asymmetric unit, Na⁺ is coordinated to the hydroxide.

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

Complex	$E_{1/2}$ (V vs Fc^+/Fc)
$[\text{K}(\text{18-crown-6})]_3[\text{SO}_3\text{LCuOH}]$ (4a)	−0.135
$[\text{NMe}_3\text{LCuOH}]\text{BArF}_4$ (5a)	0.140
$[\text{NBu}_4][\text{pyrLCuOH}]$ (1a) ^b	−0.076
$[\text{NBu}_4][\text{NO}_2\text{LCuOH}]$ (1b) ^b	0.124
$[\text{NBu}_4][\text{pipLCuOH}]$ (1c) ^b	−0.260

^aConditions: 2 mM analyte in DFB solvent, 0.2 M Bu_4NPF_6 (0.2 M $\text{Bu}_4\text{NBArF}_4$ in case of **5a**).^bFrom ref 3.

Table 3.BDE Values for $[\text{CuOH}_2]^{2+}$ Complexes

supporting ligand	solvent	BDE (kcal/mol)	ref
SO_3L^{4-}	DFB	$\sim 91^a$	this work
	H_2O	~ 87	this work
NMe_3L	DFB	$\sim 91.5^a$	this work
	H_2O	~ 91	this work
pyrL^{2-}	THF	90 ± 3	4
NO_2L^{2-}	DFB	91 ± 3	4
pipL^{2-}	THF	88 ± 3	4

^a Approximate value, see text.

Table 4.

Thermodynamic and Kinetic Data for HAT Reactions of $[\text{Cu}(\text{OH})_2]^{2+}$ Complexes with 9,10-Dihydroanthracene (DHA) and 1,4-Cyclohexadiene (CHD) at $-25\text{ }^\circ\text{C}$ in DFB

compound	ligand	BDE_{DHA} (kcal mol ⁻¹) ^a	k_{DHA} (M ⁻¹ s ⁻¹)	$k_{\text{H}}/k_{\text{D}}$ (DHA)	k_{CHD} (M ⁻¹ s ⁻¹)	BDE_{CHD} (kcal mol ⁻¹) ^a
8a	SO_3L^{4-}	14.7	400(22)	12	70(8)	15
8a' ^b	SO_3L^{4-}	14.7	500(30)	–	90(9)	15
9a	NMe_3L	14.7	2.8(7)	18 ^c	28(2)	15
2a ^d	pyL^{2-}	13.7	50(8)	27 ^e	38(2) ^f	14
2b ^d	NO_2L^{2-}	14.7	346(50)	10 ^e	–	15
2c ^d	pipL^{2-}	11.7	25(4)	17 ^e	–	12

^a Calculated as the difference between the O–H BDE of the product $[\text{Cu}(\text{OH})_2]^{2+}$ complex and the BDE of the substrate C–H bond (taken from ref 30).

^b 100 eq. of $[\text{Na}(15\text{-crown-5})]\text{OTf}$ 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 CH_2Cl_2 .

^f From ref 31.