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Formation of hybrid guanidine-stabilized bis(μ -oxo)dicopper cores in solution: Electronic and steric perturbations

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Abstract

A series of new hybrid peralkylated-amine-guanidine ligands based on a 1,3-propanediamine backbone and their Cu-O₂ chemistry is reported. The copper(I) complexes react readily with O₂ at low temperatures in aprotic solvents with weakly coordinating anions to form exclusively bis(μ -oxo) dicopper species (**O**). Variation of the substituents on each side of the hybrid bidentate ligand highlights that less sterically demanding amine and guanidine substituents increase not only the thermal stability of the formed **O** cores but enhance inner-sphere phenolate hydroxylation pathways. TD-DFT analysis on selected guanidine-amine **O** species suggest that the additional visible feature observed is a guanidine $\pi^* \rightarrow \text{Cu}_2\text{O}_2$ LMCT, which appears along with the classic oxo- $\zeta_{\text{u}}^* \rightarrow \text{Cu(III)}$ and $\pi_{\zeta}^* \rightarrow \text{Cu(III)}$ LMCT transitions.

Keywords

Copper; Dioxygen; Guanidine Ligands; Density Functional Theory; UV/Vis-Spectroscopy

Introduction

Many copper enzymes in nature directly activate O₂ to perform a myriad of essential chemical transformations almost exclusively performed with this metal.^[1–6] Tyrosinases (Ty), ubiquitously found in both eukaryotes and prokaryotes, are well recognized examples that perform the first committed step in the synthesis of melanine from tyrosine by catalytic hydroxylation of the phenol to a catechol.^[4–6] Recent crystal structures of oxygenated tyrosinase (oxyTy) confirmed a binuclear copper(II) μ - η^2 : η^2 -peroxo species (**SP**)^[7] anticipated from earlier spectroscopic and modeling studies.^[6] Given the unique and impressive catalytic oxidation chemistry of tyrosinases, decades of effort have been directed

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Supporting Information Available:

Eyring plots for thermal decomposition of [2b]²⁺, [3b]²⁺, [4b]²⁺, [6b]²⁺ and [7b]²⁺, FcCOOH titration of [3b]²⁺ and [7b]²⁺ and input coordinates for hybrid DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

to reproduce their reversible dioxygen binding and oxidative reactivity in small synthetic complexes.^[1–6, 8–15] Synthetic ligand systems that integrate electron-rich amine ligating groups in place of imidazoles can form side-on peroxide species exclusively, but more commonly an isomeric species, a bis-oxide-bis-Cu(III) complex (**O**), is formed presumably due to the stronger σ -donating character of the amines compared to imidazole nitrogen ligating groups.^[8,9,16] In a limited number of cases, the side-on peroxide and bis-oxide species exist in a facile equilibrium at low temperatures, which supports the notion that the energetic difference between the two isomeric forms can be small.^[8,17] In fact, the position of such equilibria is sensitive to the nature of weakly coordinating counter-anions in solution; full conversion of an optically pure **O** species with SbF₆ counter-anions to a **SP** species is possible by the simple addition of one equivalent of a more coordinating anion, consistent with specific anionic binding to the less-compact **SP** species.^[18,19] As the position of this equilibrium is sensitive to anions, it is not surprising that phenolate ligation to a **SP** species is capable of triggering isomerization to an **O** species with a phenolate bonded in an equatorial position. Such positioning can lead to phenol hydroxylation.^[20–22] As optically characterized **O**^[20–25] and **SP** species^[26–38] are reported with hydroxylating reactivity, it is unknown whether a single species is the hydroxylating agent or both are capable of such oxidation reactions.

The nature of the nitrogen ligand plays a key function in determining whether an **O** or **SP** isomer is formed.^[1–6, 8–15] Many ligand families such as tris(pyrazolyl)borates,^[39] poly(pyrazolyl)-methanes,^[35,40,41] alkyl amines,^[42] pyridines,^[43] ketiminates^[44] and guanidines,^[24,45–50] and now histamines^[51,52] have been investigated. Electron-rich bidentate ligands capable of adopting a planar, four-coordinate d⁸ Cu(III) center generally stabilize an **O** species if sufficient steric demands exist in the ligand framework to prevent formation of an unreactive copper(I) bis-chelated complex.^[53,54] Exclusive primary amine ligation is now known to stabilize **O** species, albeit formed through a core capture synthesis rather than direction oxygenation of a copper(I) precursor.^[55] In the best case, the ideal precursor copper(I) complexes are three-coordinate with a weakly associated anion or solvent molecule (*e.g.* acetonitrile). Such complexes allow for facile access of O₂ to the copper center and rapid dimerization to an **O** species formation. The resulting **O** species are very compact with Cu–Cu distances in the range of 2.73–2.85 Å.^[53,54]

In an earlier study,^[24] we compared the hybrid bidentate chelates containing one basic guanidine donor in combination with a tertiary amine to their symmetric bis-guanidine and bis-alkylated amine parental ligands. All these Cu(I) complexes oxygenate to **O** species, yet only the hybrid ligand exhibited hydroxylation of phenolates at low temperature; the other complexes only exhibited radical phenolate-coupling or ligand self-oxidation. A subtle balance exists between phenolate hydroxylation, presumably an inner-sphere process, and phenoxyl radical chemistry. In the present study, a series of seven hybrid-ligand Cu(I) complexes based on a 1,3-propanediamine backbone are investigated for their reactivity with dioxygen. Systematic variation of the guanidine and amine substituents on the ligands highlights their influence on the donor capacity and optical spectroscopy along with probing the role of steric demands on the oxidation of phenolate substrates.

Results

Ligand synthesis

The guanidine-amine-hybrid ligands $^1\mathbf{L} - ^7\mathbf{L}$ (Scheme 1 and Table 1) were synthesized by conversion of an amine to a guanidine through the reaction with a chloroformamidinium chloride (Scheme 2), which is accessible in good yields from the appropriately substituted urea and phosgene.^[56,57] The copper(I) complexes $[\mathbf{1a}]^+ - [\mathbf{7a}]^+$, with the general formula $[(\mathbf{L})\text{Cu}^{\text{I}}]^{1+}$ ($\mathbf{L} = ^1\mathbf{L} - ^7\mathbf{L}$, Table 1), were available directly by reacting equimolar amounts of $[\text{Cu}^{\text{I}}(\text{MeCN})_4]^{1+}$ and the ligand in MeCN under N_2 at ambient temperature (RT). The triflate counteranion (CF_3SO_3^-) was used throughout this study unless indicated otherwise.

Oxygenation of $[\mathbf{1a}]^+ - [\mathbf{7a}]^+$

In situ prepared, concentrated solutions of $[\mathbf{1a}]^+ - [\mathbf{7a}]^+$ were injected into preoxygenated solvents (1 atm O_2) to create $[\mathbf{1b}]^{2+} - [\mathbf{7b}]^{2+}$ ($[\text{Cu}] = 0.5\text{--}4\text{ mM}$), which all possess intense charge transfer (CT) bands near 300 and 400 nm ($\epsilon \sim 16\text{ mM}^{-1}\text{ cm}^{-1}/\text{Cu-dimer}$) and a weaker CT band near 440 nm ($\epsilon \sim 8\text{ mM}^{-1}\text{ cm}^{-1}$) (Figure 1, Table 2). The similarities of the absorption band shapes and intensities of $[\mathbf{1b}]^{2+}$, a previously characterized **O** species with exclusive guanidine ligation,^[24] to those of $[\mathbf{2b}]^{2+} - [\mathbf{7b}]^{2+}$ are consistent with exclusive **O** species formation. The incorporated O_2 in $[\mathbf{2b}]^{2+} - [\mathbf{7b}]^{2+}$ is not removed by cycles of evacuation and purging with N_2 , in line with the physical attributes of $[\mathbf{1b}]^{2+}$ and other **O** species.^[23,24,49,58] The visible CT bands of $[\mathbf{3b}]^{2+}$ and $[\mathbf{4b}]^{2+}$ are more distinct and intense than those of $[\mathbf{1b}]^{2+}$ and $[\mathbf{2b}]^{2+}$.

Spectrophotometric titrations with ferrocene monocarboxylic acid

The degree of **O** species formation of $[\mathbf{1b}]^{2+}$, $[\mathbf{3b}]^{2+}$, $[\mathbf{5b}]^{2+}$ and $[\mathbf{7b}]^{2+}$ were quantified by spectrophotometric titrations using ferrocene monocarboxylic acid (FcCOOH), a method validated by titration of other **O** species, *e.g.* $[\mathbf{1b}]^{2+}$.^[24] FcCOOH is a one electron, one proton donor with a weak OH bond dissociation energy (BDE, 72 kcal mol^{-1}).^[24] Two equivalents are required to convert an **O** species stoichiometrically to a corresponding bis-(μ -hydroxo)dicopper complex, the presumed thermodynamic product.^[24] Titrations were monitored by the disappearance of the LMCT features near 400 nm, as neither the resulting copper products nor the ferrocenium carboxylate product appreciably absorb in that range (Figure 1d).

Optical titrations of $[\mathbf{3b}](\text{CF}_3\text{SO}_3)_2$ with FcCOOH required slightly greater than 1.9 equivalents per dimer and show a linear change of absorbance with added titrant under anaerobic conditions (Figure S1); more than 2 equivalents are required if excess dioxygen is not removed. Titration of $[\mathbf{3b}](\text{CF}_3\text{SO}_3)_2$ compared to $[\mathbf{3b}](\text{SbF}_6)_2$ required five times longer to achieve equilibrium in each step; in general, the CF_3SO_3 salts required greater equilibration times. Titrations indicate greater than 95% formation of $[\mathbf{3b}](\text{CF}_3\text{SO}_3)_2$ and $[\mathbf{3b}](\text{SbF}_6)_2$ and 80% formation of $[\mathbf{7b}]^{2+}$ (Figure S2). Similar titrations of $[\mathbf{1b}]^{2+}$ previously indicated greater than 95% formation. $[\mathbf{2b}]^{2+}$, $[\mathbf{4b}]^{2+}$ and $[\mathbf{6b}]^{2+}$ were not titrated with FcCOOH as their thermal decays at 195 K are significant in the required titration time.

Thermal decomposition in solution

The thermal decomposition kinetics of $[1b]^{2+} - [7b]^{2+}$ were studied by UV-Vis spectroscopy. Solutions of $[1b]^{2+} - [7b]^{2+}$ ($[Cu] \sim 1-2$ mM, THF, 195 K) were formed as described above and the excess O_2 was removed by cycles of evacuation and purging with N_2 . Each solution was warmed rapidly to a particular temperature, and the time-dependent evolution of optical features at a single wavelength was analyzed to provide a decomposition rate constant (k_{obs}). The decay activation parameters from an Eyring analysis in the 213 – 273 K range (Table 2) support that the thermal decomposition is not influenced significantly by choice of counter-anions, *e.g.* similar activation parameters of $[1b](CF_3SO_3)_2$ and $[1b](SbF_6)_2$ in THF are measured.^[24]

The thermal decay products of $[1b]^{2+} - [7b]^{2+}$ were analyzed by GC and GC-MS, after an aqueous work-up of $[1b]^{2+} - [7b]^{2+}$. The parent ion of the intact ligand was not observed and unknown fragments of low molecular weight were observed, but could not be identified. Dealkylation of amine ligating groups is a common thermal decay pathway for **O** complexes.^[16,58–60] Indeed, ligand de-ethylation could be inferred through the iodoform colorimetric analysis for acetaldehyde.^[61] $[2b]^{2+}$, $[4b]^{2+}$ and $[6b]^{2+}$ containing NEt_2 groups gave a positive iodoform test, while $[1b]^{2+}$ and $[3b]^{2+}$ with NMe_2 groups gave a negative test. As $[3b]^{2+}$ with NMe_2 and ethyl substituents on the guanidine subunit gave a negative test, de-ethylation occurs from a NEt_2 group. The activation enthalpies of NMe_2 containing complexes, $[1b]^{2+}$ and $[3b]^{2+}$, are significantly higher than those for NEt_2 containing complexes, $[2b]^{2+}$ and $[4b]^{2+}$, consistent with weaker methylene C–H BDE of a NEt_2 group.

Theoretical Investigation

The ligand to metal charge transfer (LMCT) features in the visible range of $[1b]^{2+} - [7b]^{2+}$ are sensitive to the steric demands of the guanidine alkyl substituents, presumably arising from differential orientation of the guanidine planes relative to the Cu_2O_2 core. The intra-guanidine twists, the dihedral angles between the four-atom $N_{amine}C_3$ -planes and the four atom $C_{gua}N_3$ -plane (Figure 2a), are observed in X-ray crystal structures of both metal-coordinated guanidines^[47,62] and uncoordinated guanidines.^[63,64] These twists result from steric interactions between adjacent guanidine NMe_2 -groups. Smaller twists allow for greater delocalization and stabilization of the guanidine π system.

The interplay of these twist angles with metal ligation of the guanidine nitrogen impacts the electronic communication between the guanidine π -system and the copper centers. As DFT calculations at a B3LYP/2z level of theory well reproduce the experimental bond lengths and trends in key metrical parameters observed among the guanidine/amine **O** complexes,^[25,50] similar constrained optimization calculations were performed with fixed $N=C-N-C(Me)$ dihedral angles between 10 and 50° for $[1b]^{2+}$. The metrical parameters for 5 conformers are collected in Table 3.

The fixed $N=C-N-C$ dihedral angle within the guanidine units induce structural changes in the copper coordination and Cu_2O_2 core. With increasing dihedral angle (i) the $Cu-N_{gua}$ bond length increases, (ii) the $Cu-N_{amine}$ bond shortens, (iii) the $Cu...Cu$ vector shortens, (iv) the $C=N$ bond length shortens, and (v) the $C-N_{gua-amine}$ bonds elongate. Accordingly,

delocalization within the guanidine unit increases with decreasing guanidine twist, manifest in a lengthening of the C=N double bond. TD-DFT calculations on each conformer predict electronic LMCT transitions of high intensity near 300 nm, coinciding with an $\text{oxo}-\pi^* \rightarrow \text{Cu}_2\text{O}_2$ transition (Table 4 and Figure 3). These features red-shift significantly with increasing guanidine twist along with emergence of an additional feature in the visible range near 450 nm.

The features near 300 and 350 nm correspond to the classical transitions of an **O** species ($\text{oxo}-\zeta_{\text{u}}^* \rightarrow \text{Cu(III)}$ and $\pi_{\text{c}}^* \rightarrow \text{Cu(III)}$ LMCT).^[24,66] The accepting molecular orbitals (LUMO & LUMO+1) are best understood as the anti-bonding combination of the ligand σ -bonding interactions, including both oxygen and the nitrogen atoms with the copper d_{xy} orbitals. The transitions are not altered in overall character with twisting, but red-shift due to lower accepting and raised donating orbitals, both a manifestation of lesser guanidine bonding to the copper centers (Figure 4). This lesser donation correlates to a smaller calculated proton affinity for the free **1L** in the constrained conformation for each twist angle.

The new LMCT absorption feature near 450 nm involve a guanidine π^* orbital to LUMO+1 transition. At a 10° twist angle, this transition has limited intensity that increases with greater localization of the guanidine π -system associated with a greater twist. The increase in the guanidine N 2p character in the donor MO and in the overlap with the Cu_2O_2 core accepting molecular orbital allow for greater absorption intensity.^[67,68] The red-shift of the transition appears to result primarily from a stabilization of the LUMO+1 accepting orbital.

Tetraethylguanidine units significantly impact the spectroscopic features of the resulting **O** species compared to tetramethylguanidine units, presumably from larger guanidine twist angles in the lowest energy conformation. Unfortunately, no single crystal x-ray structure of a copper complex with a tetraethylguanidine unit is available to provide a structural benchmark for the twist angles or conformation of the ethyl substituents. Computationally, the lowest energy conformation of **[3b]²⁺** found is correlated with the smallest average guanidine twist of 38° , which is greater than that found for the most stable conformation of **[1b]²⁺** at 33.5° . The red-shifting of the experiment and computational spectra of **[3b]²⁺** relative to **[1b]²⁺** support a greater twist angle in **[3b]²⁺** as compared to **[1b]²⁺**.

Reactivity with phenolates

The oxidative reactivity of **[1b]²⁺**, **[3b]²⁺**, **[5b]²⁺** and **[7b]²⁺** was examined with 2 equivalents of 2,4-ditertbutylphenolate. The reactions were monitored optically at 195 K until either the characteristic CT feature near 400 nm was quenched or 6 h had elapsed. After an acidic workup, the organic products were assayed by ^1H NMR spectroscopy. Yields are indicated with respect to oxidizing equivalents of Cu_2O_2 core, assuming exclusive cupric products (Table 5). The fast unimolecular oxidative thermal decay of **[2b]²⁺**, **[4b]²⁺** and **[6b]²⁺** at 195 K precluded meaningful reactivity studies with phenolates. **1b** readily reacts with 2,4-ditertbutylphenolate yielding 70% of the oxygenated product 3,5-di-tert-butylcatechol (**DBCat**).^[24] Small amounts of the corresponding quinone (**DBQ**) are isolated as well. Similar oxidative behavior is observed for **[3b]²⁺**. In case of **[5b]²⁺**, the yield of the

catechol decreases to 10%. Using $[7b]^{2+}$, the yield of oxidized products is low and significant amounts of the radical coupled bis-phenol product (**CP**) are formed.

Discussion

Ligand design

The present series of hybrid guanidine ligands highlights the steric and electronic influence of the substituents on the optical spectroscopy and reactivity of formed dicopper(III)-bis(μ -oxo) species. Intra-ligand interactions within a guanidine unit impact the conformation of a complex exemplified by $[1b]^{2+}$ and $[3b]^{2+}$; small angular variations within the guanidine group influence its donor strength. Comparison of the 400 nm features of the **O** species formed with Me_2N and Et_2N -containing hybrid ligands shows a clear red-shift correlated to larger guanidine substituents ($[1b]^{2+}$ – $[4b]^{2+}$; Table 2). An additional LMCT feature in the visible range exists for these hybrid ligand **O** species that shifts to lower energy with increasing substituent steric demand; this shifting is most sensitive to the guanidine substituents.

Anion impact

The titration of several **O** complexes with guanidine-amine hybrid ligands with ferrocene monocarboxylic acid shows clearly a near quantitative formation from their Cu(I) starting materials. The $FcCOOH$ titrations of $[3b]^{2+}$, $[5b]^{2+}$ and $[7b]^{2+}$ suggest tight ion pairing in solution, as a change in the weakly coordinating counter-anion can slow the reaction rate upto 5-fold in the case the triflate salts of $[1b]^{2+}$ and $[3b]^{2+}$ compared to their hexafluoroantimonate counterparts. Assuming a direct proton coupled electron transfer (PCET) from $FcCOOH$ to an oxygen atom of a Cu_2O_2 core, tighter anion association to the complex (*e.g.* triflate) should impede direct access to the core.

Thermal Decay

While **O** species with Me_2N containing ligands ($[1b]^{2+}$, $[3b]^{2+}$) require higher temperatures to measure their thermal decay rates, the related complexes with Et_2N containing ligands ($[2b]^{2+}$, $[4b]^{2+}$) decay with half-lives between 14 to 3 min at 193 K, depending on the guanidine substituents. As all decay processes fit a first order process, it is assumed that the predominant thermal decay pathway involves intramolecular ligand oxidation, common among **O** species.^[9,58] The systematic variation of the ligand substituents in $[1b]^{2+}$ – $[4b]^{2+}$ correlates NEt_2 groups with lesser thermal stability. De-ethylation occurs presumably through methylene hydroxylation of a NEt_2 group and release of acetaldehyde upon workup. Positive iodoform tests for acetaldehyde for the decay products of $[2b]^{2+}$ and $[4b]^{2+}$, but not for $[3b]^{2+}$, supports selective de-ethylation of NEt_2 groups. The enhanced thermal stability of the NMe_2 containing ligands presumably results from the *ca.* 2–3 kcal mol^{–1} greater C–H BDE of a methylamine as compared to a methylene C–H of an ethylamine group; selective de-ethylation of a $NMeEt$ group from an **O** species has been reported previously.^[53] Though the presence of formaldehyde was not confirmed, the presumed decay pathway for $[1b]^{2+}$, $[3b]^{2+}$, $[5b]^{2+}$ and $[7b]^{2+}$ presumably occurs by a similar hydroxylation of a NMe_2 group.

Theoretical studies

DFT calculations twisted congeners of $[1b]^{2+}$ reveal a clear change of bonding within the guanidine group: greater twisting results in a loss in guanidine basicity and donating ability to the metal center. An analysis of the CT absorption feature near 450 nm by TD-DFT suggest a guanidine π^* orbital to the LUMO+1 transition. At a 10° twist, this guanidine π^* orbital is not as pronounced compared to 50° , where this orbital gains considerable contribution due to lesser guanidine delocalization. Simultaneously, the antibonding LUMO+1 is stabilized with increasing twist due to lesser bonding and antibonding interactions, which leads to lower energy optical transitions. The increase in intensity results from the more favorable overlap of the guanidine π^* orbital with the LUMO+1. Hence, an understanding of the nature of the π_{gua}^* -Cu₂O₂ transition allows subtle conformational preferences of the ligands.

The DFT optimization analysis of $[3b]^{2+}$ suggests greater twist angles for the guanidine units than in $[1b]^{2+}$. Absent steric demands, a guanidine system prefers a more planar conformation and delocalization; it is the steric demands of the substituents on the guanidine that reduce this delocalization. In recent work, x-ray crystal structures of tetraethylguanidine-pyridine zinc provide insights into low energy conformers of the ligand.^[62] The tetraethylguanidine systems show larger twist angles than their tetramethylguanidine counterparts. Hence it is consistent that $[3b]^{2+}$ exhibits a more intensive and more red-shifted sideband (“guanidine band”) than $[1b]^{2+}$ in the experimental and calculated UV/Vis spectra.

Hydroxylation chemistry

The close similarity of the seven ligands in this investigation and the differential thermal stability and phenolate reactivity of their **O** species is striking. Though 1-electron outer-sphere reduction potentials for these complexes by traditional methods are not accessible through standard low temperature potentiometry, we assume that the ligand variations do not change significantly their thermodynamic potentials but only the kinetic barriers of different reaction pathways. $[3b]^{2+}$ is an efficient phenolate to catecholate hydroxylation reagent with yields greater than 65%, comparable to other reactive reported **O** species.^[23] Facile phenolate binding to an axial Cu(III) position, followed by ligand rearrange to position the phenolate equatorially, and finally electrophilic attack of the phenolate π -system is one potential mechanism for hydroxylation with such an **O** species.^[20–22] The significant decrease in overall catecholate yield with $[5b]^{2+}$ and $[7b]^{2+}$ is a curious result, as the attenuated yields can not be attributed simply to increased steric demands of the ligands; though $[5b]^{2+}$ and $[7b]^{2+}$ do contain more atoms than $[3b]^{2+}$, the effective steric demands of ethyl substituents ($[3b]^{2+}$) are equivalent if not larger than for the ligands containing 6-membered ring substituents when assessing the Cu₂O₂ core. Yet, in the case of $[5b]^{2+}$ and $[7b]^{2+}$, the percentage of radical coupled phenolates increases significantly compared to $[3b]^{2+}$. We postulate that this differential product distribution results from a lesser ligand flexibility of $[5b]^{2+}$ and $[7b]^{2+}$ thereby raising the ligand reorganization energy to appropriately position of a ligated phenolate for efficient hydroxylation. In these latter two cases, one-electron oxidation of the phenolate, either by an inner or outer sphere process, becomes competitive, releasing a phenoxyl radical, which can couple in solution.^[24]

Conclusions

A series of closely related guanidine-amine hybrid ligands and their copper-dioxygen complexes provide insights into ligand design features that enhance their thermal stability so that their oxidizing capacity can be directed productively to external substrates. As previously documented and reaffirmed through this investigation, the weakest C–H bond of an alkyl amine substituent that ligate a Cu(III) center of an **O** species are oxidized readily, presumably through a hydroxylation pathway. This reactivity is understood clearly from computational studies identifying the lowest energy C–H activation pathway along the O–O vector of the **O** Cu₂O₂ core; alkyl substituents of amines with stronger C–H BDE, such as methyl groups, provide not only enhanced thermal stability of the **O** species, but also inhibit substrate access to the core the least.^[55] The guanidine stabilization of **O** species is consistent with their stronger basicity, greater than a peralkylated amine. Variation of guanidine substituents with associated differential twisting alters its delocalization, which impacts its ability to interact with the Cu₂O₂ core. TD-DFT calculations suggest that the new visible band in these complexes as a CT transition from the guanidine to the Cu₂O₂ core. Finally, we suggest that phenolate hydroxylation by these hybrid-ligand **O** species requires a balance of substrate access to the Cu₂O₂ core along with ligand flexibility, as the symmetric parent ligands only exhibit radical coupling chemistry with phenolates at 195 K.^[24]

Experimental

Caution! Phosgene is a severe toxic agent and extensive exposure may be lethal. Use only in a well-ventilated fume hood.

Materials

All manipulations were performed under pure dinitrogen (N₂), which was dried over granulate P₄O₁₀, using Schlenk techniques or in a glovebox. Solvents (Fisher Scientific) were distilled from Na-benzophenone ketyl radical (THF, Et₂O) or from CaH (MeCN, CH₂Cl₂). Dry NaH was obtained by oil removal from a 60% dispersion (Aldrich) with dry hexane and dried in vacuo. [Cu^I(MeCN)₄](X) (X = CF₃SO₃[−], CH₃SO₃[−], SbF₆[−]) were all prepared from Cu₂O (Aldrich) and the corresponding HX acid (Aldrich) in MeCN, and recrystallized twice from MeCN/Et₂O.^[70] Ferrocene, ferrocene monocarboxylic acid and 2,4-di-*tert*-butylphenol (Aldrich) were either recrystallized or sublimed before use. Triethylamine (Fluka), and *N*^I,*N*^I,*N*²,*N*²-tetramethylpropyl-1,3-diamine (Aldrich) was stored over CaH₂ and purified by flash distillation under vacuum. The chloroformamidinium chlorides N,N,N',N'-tetramethylchloroformamidinium chloride, N,N,N',N'-tetraethylchloroformamidinium chloride, N,N,N',N'-dipiperidylchloroformamidinium chloride and N,N,N',N'-dimorpholinochloroformamidinium chloride were prepared according to literature procedures.^[57]

Physical measurements

Spectra were recorded with the following spectrometers: NMR: Bruker Avance 500; IR: Nicolet P510; MS (EI, 70 eV): Saturn 2; MS (CI, CH₄): Finnigan MAT 8200; MS (ESI):

Esquire 3000 Ion Trap; UV-Vis: Perkin–Elmer Lambda 45 with a low temperature fiber-optic interface (Hellma; 1 mm), or a Cary50 with a custom-designed quartz fiber-optic dip probe (Hellma; 1 or 10 mm) and a custom-designed Schlenk cell with compression fittings (ChemGlass). Microanalyses were performed with a Perkin-Elmer 2400 analyzer.

Computational methods

Density Functional Theory (DFT) calculations were performed using the Gaussian 03 program, Revision E.01.^[71] The calculations of the **O** species were performed within the restricted formalism. The geometries were optimized (Table 3) using the B3LYP functional and an all electron 6–31g(d) Pople basis set on all atoms, abbreviated as **2z**. The starting geometry supported by **¹L** was generated from its bis-(μ-hydroxo)dicopper(II) x-ray crystal structure^[24] by adjusting the Cu–Cu and O–O distances to 2.8 and 2.3 Å for an **O** isomer. The starting geometries for complexes with **³L** were generated from [**1b**]²⁺ by adding methyl groups to the guanidine substituents. [**1b**]²⁺ and [**3b**]²⁺ were optimized in *C_i* symmetry. Electronic energies were determined at a **3z** level (6-311G+(d) on Cu, N and O and 6–31G(d) on C and H); free energies were calculated from the **3z** electronic energies by inclusion of the zero-point energies and thermal corrections from the frequency calculations at the **2z** level, which were computed for each optimized structure to verify a true minimum.

Electronic spectra transitions were calculated using time dependent density functional theory (TD-DFT) with the B3LYP functional and the **3z** basis set using an IEF-PCM solvation model for THF ($\epsilon = 7.58$) and a Pauling radii scheme. The contributions of atomic orbitals to major donor and acceptor molecular orbitals were determined using Mulliken population analysis as implemented AOMix^[67,68] and using the NBO software as implemented in Gaussian03 Rev. E01^[71,72] For the calculations of the relative proton affinity, an isodesmic reaction between the 50°, 30° and 10° conformers of ligand **¹L** and its guanidine-protonated congeners was set up and the relative energies were calculated.^[73]

General synthesis of guanidine-amine hybrid ligands

A solution of the chloroformamidinium chloride (40 mmol) in dry MeCN was added dropwise under vigorous stirring to an ice-cooled solution of an amine (40 mmol) and triethylamine (40 mmol) in dry MeCN. After 3 – 4 h at reflux, an aqueous solution of NaOH (40 mmol) was added. The solvent and NEt₃ were evaporated under vacuum. In order to deprotonate the guanidine hydrochloride, 50 wt. % KOH (*aq.*, 15 mL) was added and the free base was extracted into the MeCN phase (3 × 30 mL). The organic phase was dried with Na₂SO₄, filtered, and removed under reduced pressure.

2-(3-(Diethylamino)propyl)-1,1,3,3-tetramethylguanidine (Et₂LG^{Me4}, **2L**)

Yellow oil, yield: 8.69 g = 38.1 mmol = 95 %. **¹H-NMR** (500 MHz, CDCl₃, 25°C, δ [ppm]): 0.93 (m, 6H, CH₃, ³J = 7.15 Hz), 1.55–1.61 (m, 2H, CH₂), 2.39–2.45 (m, 6H, CH₂), 2.56 (s, 6H, CH₃), 2.65 (s, 6H, CH₃), 3.02–3.04 (t, 2H, CH₂, ³J = 6.65 Hz). **¹³C-NMR** (125 MHz, CDCl₃, 25 °C, δ [ppm]): 11.8 (CH₃), 29.6 (CH₂), 38.7 (CH₃), 39.5 (CH₃), 47.0 (CH₂), 47.8 (CH₂), 50.9 (CH₂), 159.9 (C_{Gua}). **EI-MS** (m/z, (%)): 228.2 (31) [M⁺], 199 (63) [M⁺–CH₂CH₃], 157 (19), 142 (71) [M⁺–H₂C–N(CH₂CH₃)₂], 129 (46), 128 (20) [M⁺–H₄C₂N(CH₂CH₃)₂], 114 (10), 113 (14), 98 (31), 97 (44), 86 (100) [H₂CN(CH₂CH₃)₂]⁺, 85

(90), 71 (31), 58 (15), 42 (12). **IR** (Film between NaCl plates, $\tilde{\nu}$ [cm⁻¹]): 2968 *m*, 2933 *m*, 2871 *m*, 2837 *m*, 2798 *m*, 1655 *w*, 1624 *vs* (ν (C=N)), 1496 *m*, 1452 *m*, 1402 *vw*, 1365 *s*, 1311 *vw*, 1248 *w*, 1234 *w*, 1200 *vw*, 1165 *vw*, 1134 *m*, 1109 *vw*, 1066 *w*, 1009 *vw*, 991 *w*, 914 *vw*. Anal. Calcd for C₁₂H₂₈N₄: C 63.11, H 12.36, N 24.53. Found: C 62.88, H 12.67, N 24.81.

2-(3-(Dimethylamino)propyl)-1,1,3,3-tetraethylguanidine (^{Me}₂LG^{Et}₄, ³L)

Yellow oil, yield: 9.12 g = 35.6 mmol = 89 %. **¹H-NMR** (500 MHz, CDCl₃, 25 °C, δ [ppm]): 0.95–0.99 (m, 12H, CH₃), 1.61–1.67 (m, 2H, CH₂), 2.16 (s, 6H, CH₃), 2.24–2.27 (m, 2H, CH₂), 2.96 (q, 4H, CH₂, ³J = 7.1 Hz), 3.05–3.10 (m, 6H, CH₂). **¹³C-NMR** (125 MHz, CDCl₃, 25 °C, δ [ppm]): 13.0 (CH₃), 13.6 (CH₃), 30.8 (CH₂), 41.5 (CH₂), 42.6 (CH₂), 45.5 (CH₃), 48.0 (CH₂), 58.4 (CH₂), 158.2 (C_{Gua}). **EI-MS** (m/z, (%)): 256.3 (52) [M⁺], 241 (17) [M⁺-CH₃], 198 (60) [M⁺-H₂CN(CH₃)₂], 185 (54), 184 (60) [M⁺-H₄C₂N(CH₃)₂], 172 (23), 127 (40), 125 (65), 114 (72), 113 (81), 100 (55), 86 (64) [H₆C₃N(CH₃)₂]⁺, 85 (72), 72 (100) [H₄C₂N(CH₃)₂]⁺, 71 (57), 70 (51), 58 (77) [CH₂N(CH₃)₂]⁺, 57 (53), 44 (41), 43 (40), 42 (41). **IR** (Film between NaCl plates, $\tilde{\nu}$ [cm⁻¹]): 2966 *s*, 2931 *s*, 2868 *m*, 2812 *m*, 2762 *m*, 1610 *vs* (ν (C=N)), 1460 *m*, 1402 *m*, 1375 *m*, 1356 *w*, 1340 *w*, 1302 *w*, 1261 *s*, 1221 *w*, 1174 *vw*, 1153 *vw*, 1132 *m*, 1097 *w*, 1070 *m*, 1041 *w*, 1011 *vw*, 968 *vw*, 930 *vw*. Anal. Calcd for C₁₄H₃₂N₄: C 65.57, H 12.58, N 21.85. Found: C 65.29, H 12.82, N 22.05.

2-(3-(Diethylamino)propyl)-1,1,3,3-tetraethylguanidine (^{Et}₂LG^{Et}₄, ⁴L)

Yellow oil, yield: 10.64 g = 37.4 mmol = 94 %. **¹H-NMR** (500 MHz, CDCl₃, 25 °C, δ [ppm]): 0.99–1.03 (m, 18H, CH₃), 1.64–1.70 (m, 2H, CH₂), 2.47–2.54 (m, 6H, CH₂), 3.01 (q, 4H, CH₂, ³J = 7.1 Hz), 3.07–3.14 (m, 6H, CH₂). **¹³C-NMR** (125 MHz, CDCl₃, 25 °C, δ [ppm]): 11.8 (CH₃), 13.0 (CH₃), 13.7 (CH₃), 29.5 (CH₂), 41.4 (CH₂), 42.7 (CH₂), 47.0 (CH₂), 48.2 (CH₂), 51.2 (CH₂), 158.3 (C_{Gua}). **EI-MS** (m/z (%)): 284.3 (71) [M⁺], 255 (94) [M⁺-CH₂CH₃], 213 (19), 198 (97) [M⁺-CH₂N(CH₂CH₃)₂], 185 (40), 184 (17) [M⁺-H₄C₂N(CH₂CH₃)₂], 182 (25), 172 (12), 156 (31), 142 (19), 127 (32), 125 (89), 114 (100) [H₆C₃N(CH₂CH₃)₂]⁺, 113 (100), 98 (50), 86 (95) [CH₂N(CH₂CH₃)₂]⁺, 85 (81), 84 (81), 72 (94) [N(CH₂CH₃)₂]⁺, 58 (37), 56 (31), 42 (21). **IR** (Film between NaCl plates, $\tilde{\nu}$ [cm⁻¹]): 2968 *vs*, 2931 *s*, 2870 *m*, 2831 *w*, 2798 *w*, 1612 *vs* (ν (C=N)), 1460 *m*, 1402 *m*, 1375 *s*, 1340 *m*, 1300 *w*, 1261 *s*, 1221 *w*, 1203 *w*, 1165 *vw*, 1134 *m*, 1070 *m*, 1011 *vw*, 926 *vw*, 914 *vw*. Anal. Calcd for C₁₆H₃₆N₄: C 67.55, H 12.75, N 19.69. Found: C 67.59, H 12.94, N 20.03.

N¹-(Dipiperidin-1-ylmethylene)-N³,N³-dimethylpropan-1,3-diamine (^{Me}₂LG^{Pip}₂, ⁵L)

Yellow oil, yield: 9.63 g = 34.4 mmol = 86 %. **¹H-NMR** (500 MHz, CDCl₃, 25 °C, δ [ppm]): 1.29–1.33 (m, 12H, CH₂), 1.44–1.50 (m, 2H, CH₂), 1.96 (s, 6H, CH₃), 2.05–2.08 (m, 2H, CH₂), 2.79–2.83 (m, 8H, CH₂), 2.90–2.92 (m, 2H, CH₂). **¹³C-NMR** (125 MHz, CDCl₃, 25 °C, δ [ppm]): 24.6 (CH₂), 25.6 (CH₂), 30.0 (CH₂), 45.3 (CH₃), 46.8 (CH₂), 47.7 (CH₂), 48.6 (CH₂), 57.8 (CH₂), 160.0 (C_{Gua}). **EI-MS** (m/z, (%)): 280.3 (68) [M⁺], 265 (29) [M⁺-CH₃], 222 (75) [M⁺-H₂CN(CH₃)₂], 209 (38), 197 (40), 196 (80) [M⁺-H₆C₃N(CH₃)₂], 154 (15), 139 (31), 137 (61), 126 (87), 125 (78), 112 (78), 98 (15), 86 (44)

$[\text{H}_6\text{C}_3\text{N}(\text{CH}_3)_2^+]$, 85 (78), 84 (100) $[\text{C}_5\text{H}_{10}\text{N}^+]$, 83 (32), 70 (43), 69 (88), 58 (70) $[\text{H}_2\text{CN}(\text{CH}_3)_2^+]$, 56 (54), 42 (40), 41 (72). **IR** (Film between NaCl plates, $\tilde{\nu} [\text{cm}^{-1}]$): 2933 *vs*, 2854 *s*, 2815 *m*, 2778 *w*, 1646 *s*, 1614 *vs* ($\nu(\text{C}=\text{N})$), 1558 *w*, 1442 *w*, 1411 *m*, 1371 *m*, 1347 *vw*, 1322 *vw*, 1249 *s*, 1213 *m*, 1155 *vw*, 1130 *m*. Anal. Calcd for $\text{C}_{16}\text{H}_{32}\text{N}_4$: C 68.52, H 11.50, N 19.98. Found: C 68.34, H 11.77, N 20.31.

N¹-(Dipiperidin-1-ylmethylene)-N³,N³-diethylpropan-1,3-diamine (Et²LG^{Pip2}, ⁶L)

Yellow oil, yield: 11.7 g = 37.9 mmol = 95 %. **¹H-NMR** (500 MHz, CDCl_3 , 25 °C, δ [ppm]): 0.99 (t, 6H, CH_3 , $^3J = 7.2$ Hz), 1.49–1.53 (m, 12H, CH_2), 1.61–1.66 (m, 2H, CH_2), 2.45–2.51 (m, 6H, CH_2), 2.93–2.95 (m, 4H, CH_2), 3.00–3.02 (m, 4H, CH_2), 3.12–3.15 (m, 2H, CH_2). **¹³C-NMR** (125 MHz, CDCl_3 , 25 °C, δ [ppm]): 11.9 (CH_3), 25.8 (CH_2), 26.1 (CH_2), 29.5 (CH_2), 47.0 (CH_2), 47.9 (CH_2), 48.6 (CH_2), 49.1 (CH_2), 50.9 (CH_2), 160.0 (C_{Gua}). **EI-MS** (*m/z*, (%)): 308.5 (24) $[\text{M}^+]$, 279 (28) $[\text{M}^+ - \text{CH}_2\text{CH}_3]$, 222 (38) $[\text{M}^+ - \text{H}_2\text{CN}(\text{CH}_2\text{CH}_3)_2]$, 197 (20), 196 (80), 154 (9), 137 (10), 128 (30), 126 (42), 125 (24), 113 (29), 112 (67), 86 (29) $[\text{H}_2\text{CN}(\text{CH}_2\text{CH}_3)_2^+]$, 85 (53), 84 (100) $[\text{C}_5\text{H}_{10}\text{N}^+]$, 69 (68), 58 (25), 41 (32). **IR** (Film zwischen NaCl-Platten, $\tilde{\nu} [\text{cm}^{-1}]$): 2968 *m*, 2931 *vs*, 2850 *m*, 2823 *m*, 1647 *m*, 1616 *s* ($\nu(\text{C}=\text{N})$), 1558 *vw*, 1541 *vw*, 1522 *vw*, 1506 *vw*, 1466 *w*, 1441 *m*, 1396 *m*, 1369 *m*, 1346 *w*, 1288 *vw*, 1248 *s*, 1213 *m*, 1157 *vw*, 1130 *w*, 1105 *vw*, 1070 *vw*, 1030 *vw*, 1012 *vw*, 957 *vw*, 912 *w*. Anal. Calcd for $\text{C}_{18}\text{H}_{36}\text{N}_4$: C 70.08, H 11.76, N 18.16. Found: C 69.79, H 11.84, N 18.39.

N¹-(Dimorpholinomethylene)-N³,N³-dimethylpropane-1,3-diamine (Me²LG^{Morph2}, ⁷L)

Yellow oil, yield: 10.24 g = 36.0 mmol = 90 %. **¹H-NMR** (500 MHz, CDCl_3 , 25 °C, δ [ppm]): 1.63–1.69 (m, 2H, CH_2), 2.19 (s, 6H, CH_3), 2.26–2.29 (m, 2H, CH_2), 3.01–3.03 (m, 4H, CH_2), 3.12–3.14 (m, 4H, CH_2), 3.17 (t, 2H, CH_2 , $^3J = 6.8$ Hz), 3.63–3.65 (m, 8H, CH_2). **¹³C-NMR** (125 MHz, CDCl_3 , 25 °C, δ [ppm]): 30.7 (CH_2), 45.6 (CH_3), 47.5 (CH_2), 48.3 (CH_2), 58.1 (CH_2), 66.9 (CH_2), 157.5 (C_{gua}). **EI-MS** (*m/z*, (%)): 284.3 (45) $[\text{M}^+]$, 226 (64) $[\text{M}^+ - \text{H}_2\text{CN}(\text{CH}_3)_2]$, 215 (18), 213 (20), 200 (18), 169 (21), 139 (32), 128 (71), 127 (48), 114 (41), 100 (19), 98 (14), 86 (66) $[\text{H}_6\text{C}_3\text{N}(\text{CH}_3)_2^+]$, 85 (49), 72 (28) $[\text{H}_4\text{C}_2\text{N}(\text{CH}_3)_2^+]$, 70 (71), 58 (100) $[\text{H}_2\text{CN}(\text{CH}_3)_2^+]$, 42 (37). **IR** (Film between NaCl plates, $\tilde{\nu} [\text{cm}^{-1}]$): 2956 *m*, 2916 *m*, 2891 *m*, 2852 *s*, 2765 *m*, 1624 *vs* ($\nu(\text{C}=\text{N})$), 1539 *w*, 1456 *m*, 1392 *m*, 1360 *m*, 1300 *w*, 1263 *s*, 1230 *s*, 1176 *w*, 1147 *w*, 1115 *vs* ($\nu(\text{R}-\text{O}-\text{R})$), 1068 *w*, 1030 *m*, 987 *w*, 974 *w*, 926 *w*. Anal. Calcd for $\text{C}_{14}\text{H}_{28}\text{N}_4\text{O}_2$: C 59.12, H 9.92, N 19.70. Found: C 58.92, H 10.25, N 19.99.

Preparations of [(L)Cu^I](CF₃SO₃) and of [(L)Cu^I](SbF₆) Complexes [1a]⁺ - [7a]⁺ and of [(L)₂Cu₂O₂](CF₃SO₃)₂ and of [(L)₂Cu₂O₂](SbF₆)₂ complexes [1b]²⁺ - [7b]²⁺

Solutions for optical investigations and reactivity studies of [1b]²⁺ - [7b]²⁺ were prepared generally in situ by initially mixing equimolar amounts of $[\text{Cu}^{\text{I}}(\text{MeCN})_4](\text{CF}_3\text{SO}_3)$ or of $[\text{Cu}^{\text{I}}(\text{MeCN})_4](\text{SbF}_6)$, respectively, with **¹L-⁷L**. Oxygenation proceeded by rapid injection of a concentrated solution into a preoxygenated THF at 195 K. This “injection” method allows for the fastest and most complete formation of the **O** complexes (0.1–2 mM); generally, a 10-fold dilution of the concentrated stock solution was used.

Thermal Decomposition Kinetics

The thermal decomposition reactions of $[1b]^{2+}$, $[4b]^{2+}$, $[6b]^{2+}$, $[7b]^{2+}$ were monitored in a custom-designed low-temperature cell in THF, except where otherwise noted, with $[Cu] = 1.0$ mM. All solutions for these studies were prepared by the “injection” method to give a final volume of 5 mL. After stabilization of the optical spectrum, the excess O_2 was removed by four cycles of vacuum/ N_2 purging and the complex was allowed to decay at the desired temperature (213 – 273 K), which was maintained by a Lauda cryostat bath. Data collection for the decay started only after the solution had attained the desired temperature as detected by a low temperature thermometer inserted directly into the solution; 2 – 3 min were normally required for thermal equilibration. The absorbance at λ_{max} of feature near 390 nm was monitored to quantify the decay of $[1b]^{2+}$, $[4b]^{2+}$, $[6b]^{2+}$, $[7b]^{2+}$ and the data were fitted with a first-order kinetics model to obtain k_{obs} for each temperature. A minimum of five trials was conducted in each case. The activation parameters ($H^\ddagger$ and $S^\ddagger$) were obtained from an Eyring analysis of a linear fit of $\ln(k_{obs}T^{-1})$ against T^{-1} (see SI). In a previous study, a multi-wavelength (280 – 450 nm) component analysis of the data for **1b** was performed using SPECFIT and a first-order $A \rightarrow B$ reaction model was found to be suitable.^[24]

Oxidation of Exogenous Substrates

The reactivity of $[1b]^{2+}$, $[3b]^{2+}$, $[5b]^{2+}$ and $[7b]^{2+}$ with exogenous substrates was monitored by following the optical decay at 195 K until no further optical change was evident or 6 h. The 1.0 mM solutions of $[1b]^{2+}$, $[3b]^{2+}$, $[5b]^{2+}$ and $[7b]^{2+}$ were prepared in THF by bubbling O_2 , and the excess O_2 was removed by purging the cell with N_2 for 15 min. Sodium 2,4-di-*tert*-butylphenolate (1–20 equiv) was injected as a THF (0.5 mL) solution. The reactions were quenched with degassed H_2SO_4 (0.5 M, 2 mL), the volatiles were removed, the residue was extracted with CH_2Cl_2 , and products were analyzed by 1H NMR. The amounts of phenol, catechol, and quinone were quantified by comparison with authentic samples and a non-reactive internal standard. These experiments were completed at least three times for each **O** core.

Spectrophotometric titrations of $[3b]^{2+}$ and $[7b]^{2+}$ (195 K, THF, $[Cu] = 1.0$ mM) were conducted by successive injections of 0.2 equiv aliquots of $FcCOOH$. Equilibration was assumed when successive optical spectra did not change appreciably.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

a) Solution UV-vis spectra of $[\mathbf{1b}]^{2+}$, $[\mathbf{3b}]^{2+}$, $[\mathbf{5b}]^{2+}$ and $[\mathbf{7b}]^{2+}$ ($[\text{Cu}] = 1 \text{ mM}$, THF, 195 K, $\epsilon \text{ mM}^{-1}\text{cm}^{-1}/\text{dimer}$, CF_3SO_3^-); b) Solution UV-vis spectra of $[\mathbf{1b}]^{2+}$, $[\mathbf{3b}]^{2+}$, $[\mathbf{5b}]^{2+}$ and $[\mathbf{7b}]^{2+}$ ($[\text{Cu}] = 1 \text{ mM}$, THF, 195 K, $\epsilon \text{ mM}^{-1}\text{cm}^{-1}/\text{dimer}$, SbF_6^-); c) Solution UV-vis spectra of $[\mathbf{2b}]^{2+}$, $[\mathbf{4b}]^{2+}$ and $[\mathbf{6b}]^{2+}$ ($[\text{Cu}] = 1 \text{ mM}$, THF, 195 K, $\epsilon \text{ mM}^{-1}\text{cm}^{-1}/\text{dimer}$, CF_3SO_3^-); d) Titration of $[\mathbf{3b}](\text{SbF}_6)_2$ in 0.2 equiv steps with ferrocene monocarboxylic acid (FcCOOH) at 195 K in THF. The 635 nm absorption feature is associated with ferrocenium carboxylate. Inset: extinction coefficient at 389 nm versus the number of equiv of FcCOOH per dimer.

Figure 2.

a) Schematic representation of the p orbitals forming the π -system within a guanidine group; b) the two intra-guanidine dihedral angles (twist angles) in tetramethylguanidine ethane defined by the intersection of a red (CN₃) and grey (NC₃) plane; c) dihedral angle of the guanidine plane against the Cu₂O₂ plane in [1b]²⁺ (CN₃ vs Cu₂O₂).

Figure 3.
TD-DFT calculated UV/Vis spectra for 5 conformers of $[1b]^{2+}$ (B3LYP/3z)

Figure 4. Molecular orbitals of differentially twisted $[1b]^{2+}$ (B3LYP/2z) {^a negative proton affinity implies a more acidic guanidine nitrogen ^[69]}

Scheme 1.

Scheme 2.
Synthesis of **2L** – **5L**.

Table 1

Nomenclature of ligands and Cu complexes for this study

	R₁	R₂	L	[(L)CuI]⁺	[(L)₂CuII(μ-O)₂]²⁺
Me ₂ L ^G Me ₄	Me	NMe ₂	¹ L	[1a] ⁺	[1b] ²⁺
Et ₂ L ^G Me ₄	Et	NMe ₂	² L	[2a] ⁺	[2b] ²⁺
Me ₂ L ^G Et ₄	Me	NEt ₂	³ L	[3a] ⁺	[3b] ²⁺
Et ₂ L ^G Et ₄	Et	NEt ₂	⁴ L	[4a] ⁺	[4b] ²⁺
Me ₂ L ^G Pip ₂	Me	N(CH ₂) ₅	⁵ L	[5a] ⁺	[5b] ²⁺
Et ₂ L ^G Pip ₂	Et	N(CH ₂) ₅	⁶ L	[6a] ⁺	[6b] ²⁺
Me ₂ L ^G Morph ₂	Me	N(CH ₂) ₂ O	⁷ L	[7a] ⁺	[7b] ²⁺

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Table 2

UV-Vis features ^a, thermal decomposition data and degree of formation for [1b]²⁺ – [7b]²⁺.

	λ (nm) [e (mM ⁻¹ cm ⁻¹)]	Formation ^b	Decay rate, 253 K k_{obs} (S ⁻¹) [t _{1/2} (S)]	H [‡] (kcal mol ⁻¹) [S [‡] (cal K ⁻¹ mol ⁻¹)	Iodoform test
[1b] ²⁺	CF ₃ SO ₃ ⁻ : 297[20], 385 [18], 430 [8] SbF ₆ ⁻ : 290 [11], 386 [10], 430 [7]	> 95 %	1.3 · 10 ⁻³ [790] 1.5 · 10 ⁻³ [660]	11.5(3) [-26(1)] 13.4(1) [-18(5)]	negative
[2b] ²⁺	CF ₃ SO ₃ ⁻ : 297 [15], 392 [18], 435 [9]	n/a	6.6 · 10 ⁻² [15] ^c	6.5(5) [-38(3)]	positive
[3b] ²⁺	CF ₃ SO ₃ ⁻ : 295 [18], 389 [17], 456 [9]	> 95 %	2.2 · 10 ⁻³ [460]	12.4(3) [-21(1)]	negative
	SbF ₆ ⁻ : 296 [15], 383 [14], 448 [9]	> 95 %	n/a	n/a	
[4b] ²⁺	CF ₃ SO ₃ ⁻ : 302 [14], 399 [16], 450 [10]	n/a	0.12 [9] ^c	5.5(5) [-41(3)]	positive
[5b] ²⁺	CF ₃ SO ₃ ⁻ : 293 [14], 388 [14], 435 [7]		n/a	n/a	n/a
	SbF ₆ ⁻ : 290 [14], 387 [15], 461 [5]	70 %	n/a	n/a	
[6b] ²⁺	CF ₃ SO ₃ ⁻ : 295 [12], 390 [13], 430 [7]	n/a	0.11 [9] ^c	7.4(5) [-33(3)]	positive
[7b] ²⁺	CF ₃ SO ₃ ⁻ : 292 [11], 393 [13], 430 [7]	80 %	5.9 · 10 ⁻³ [170] ^c	2.6(7) [-59(4)]	n/a
	SbF ₆ ⁻ : 290 [13], 392 [16], 458 [4]				

^a λ_{max} (nm) [e (mM⁻¹cm⁻¹)/Cu-dimer] at 195 K without solvent contraction corrections from 298 to 195 K (ca. 10%), the band position and intensity was determined by Gaussian deconvolution.

^b Determined by back-titration with FeCOOH.

^c Extrapolated from the Eyring data.

Table 3Metrical parameters^a for constrained optimizations of [**1b**]²⁺.

N=C-N-C angle ^b	10°	20°	30°	40°	50°
Cu-N _{gua}	1.90	1.91	1.91	1.91	1.91
Cu-N _{amine}	2.01	2.01	2.01	2.00	1.99
Cu-Cu	2.77	2.77	2.77	2.76	2.76
C _{gua} =N _{gua}	1.37	1.36	1.35	1.34	1.33
C _{gua} -N _{gua,amine}	1.36	1.36	1.36	1.36	1.37
CN ₃ vs Cu ₂ O ₂	78.8	77.4	74.6	74.1	72.8
CN ₃ vs NC ₃	8.8, 11.3	18.9, 21.2	29.2, 30.9	39.8, 40.2	50.5, 49.5
NC ₃ vs NC ₃	17.8	34.9	51.2	66.7	81.6
E _{dec} (kcal mol ⁻¹) ^c	23	11	2	3	11

^aDistances in Å, angles in deg.^bFixed intra-guanidine dihedral angle.^cElectronic energy of each conformer with the fully optimized structure selected with a N=C-N-C dihedral angle of 33.5° as the reference state.

Table 4Optical transition predictions for **[1b]**²⁺ [65]

Twist	oxo- π $\rightarrow$ Cu ₂ O ₂ (oscillator strength)	oxo- σ $\rightarrow$ Cu ₂ O ₂ (oscillator strength)	$\pi^*_{\text{gua}} \rightarrow$ Cu ₂ O ₂ (oscillator strength)
10°	302 (0.41)	352 (0.24)	443 (0.01)
20°	304 (0.40)	351 (0.22)	443 (0.02)
30°	311 (0.38)	348 (0.18)	443 (0.04)
40°	318 (0.29)	349 (0.13)	443 (0.06)
50°	331 (0.22)	349 (0.11)	451 (0.07)

Table 5Reactivity of selected **O** species with 2,4-ditertbutylphenolate

O species	Yield [%]	Ratio of products^a DBCat : DBQ : CP
[1b](CF ₃ SO ₃) ₂	70	90 : 10 : 0
[1b](SbF ₆) ₂	70	95 : 5 : 0
[3b](CF ₃ SO ₃) ₂	65	90 : 10 : 0
[3b](SbF ₆) ₂	80	80 : 20 : 0
[5b](CF ₃ SO ₃) ₂	10	90 : 5 : 5
[5b](SbF ₆) ₂	20	80 : 10 : 10
[7b](CF ₃ SO ₃) ₂	30	60 : 10 : 30
[7b](SbF ₆) ₂	40	65 : 10 : 25

^aYield and product ratios determined via ¹H-NMR spectroscopy of the products obtained by acid quenching using an average of at least three trials with an internal standard.