Published in final edited form as:

Eur J Inorg Chem. 2015 December ; 2015(36): 5856–5863. doi:10.1002/ejic.201501060.

Secondary Sphere Hydrogen Bonding in Monocopper Complexes of Potentially Dinucleating Bis(carboxamide) Ligands

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Abstract

Reaction of a macrocyclic ligand precursor comprising two bis(carboxamido)pyridine units (**H₄L4**) connected by ethylene linkers with NMe₄OH and CuX₂ (X = Cl, OAc, or OTf) yielded monocopper complexes [NMe₄][(H₂L4)Cu(X)] (X = Cl (**3**), OAc (**4**), or OH (**5**)), in contrast to previous work using a related ligand with ortho-phenylene linkers wherein dicopper compounds were isolated. X-ray structures of the complexes revealed hydrogen bonding from the free carboxamide N-H groups in the doubly protonated form of the ligand (**H₂L4**⁺) to the monodentate fourth ligand coordinated to the Cu(II) ion. Similar secondary sphere hydrogen bonding interactions were identified in multinuclear compounds [NMe₄]₂[(H₂L4)Cu]_n(CO₃) (n = 2 or 3) that were isolated from exposure of **5** to air.

Cyclic voltammetry revealed oxidations of **3** and **5** at potentials ~300 mV higher than analogous monocopper complexes of bis(arylcarboxamido)pyridine ligands which lack the intramolecular hydrogen bonds, consistent with removal of electron density from the metal center by the hydrogen bonding array. Another ligand variant (**H₄L5**) with ortho-phenylene linkers and only one bis(carboxamido)pyridine moiety yielded monocopper complexes [NMe₄][(H₂L5)Cu(OAc)] • DMF (**8**) and [NMe₄][(H₂L5)CuCl)] • CH₃CN (**9**), but the X-ray structures revealed a different hydrogen bonding arrangement to the solvate molecules. Nonetheless, a high redox potential for **9** was observed, consistent with intramolecular hydrogen bonding interactions in solution.

Graphical abstract

Instead of binding two Cu(II) ions, macrocycles with two bis(carboxamido)pyridine ligands linked by ethylene units bind only one, and feature intramolecular hydrogen bonding that influences the Cu(II/III) redox potential. A purposefully mononucleating ligand with *ortho*-phenylene linkers displays a different hydrogen bonding pattern, involving carboxamido N-H interactions with solvate molecules.

Keywords

copper; hydrogen bonding; redox; macrocycles

Introduction

By understanding the properties and reactivity of copper-oxygen intermediates implicated in reactions of metalloenzymes and other catalysts, progress toward the development of new oxidation processes may be achieved.^[1] Motivated by intriguing proposals for such intermediates, including [CuO]⁺ species in enzymes such as peptidylglycine monooxygenase,^[2] dopamine β -monooxygenase,^[3] and lytic polysaccharide monooxygenase^[4] and [CuOCu]ⁿ⁺ ($n = 2-4$) species in methane monooxygenase^[5] and heterogeneous Cu-doped zeolites,^[6] we and others have targeted for synthesis and detailed study reactive mono- and dicopper complexes containing these and related cores.^[1, 7] In recent work,^[8, 9] we successfully prepared novel compounds **1** and **2** proposed to contain [Cu^{III}OH]²⁺ and [Cu^{II/III}(OH)Cu^{III}]^{4+/5+} moieties using the ligands **L1**²⁻, **L2**²⁻, and **L3**⁴⁻, respectively (Figure 1). The powerful electron donating ability of the ligand carboxamide donors was critical for stabilizing the reactive oxidized cores of these complexes.

Concerned about the potential redox noninnocence of the *ortho*-phenylenediamine linkers in **L3**⁴⁻, and with the aim of further enhancing the carboxamide electron donating properties

and thus further stabilizing oxidized copper species to enable more complete characterization, we turned to the analogous ligands **L4**⁴⁻ [10] comprising simple ethylene linkers. As we report herein, efforts to isolate dicopper complexes of **L4**⁴⁻ have failed, however, and instead we have discovered a new class of monocopper complexes that feature hydrogen bonding from the free carboxamide N-H groups in the doubly protonated form of the ligand (**H₂L4**²⁻) to the fourth ligand coordinated to the Cu(II) ion. Such interactions model secondary sphere hydrogen bonding important metalloenzyme active sites.^[11] It is understood that hydrogen bond donating and accepting residues in the second coordination sphere of enzyme active sites have an effect on the redox potential of the metal center. In previously reported enzymatic studies the direction and magnitude of a shift in potential is not always obvious with reports second-sphere residues both raising and lowering the redox potential. For instance, in Fe Superoxide Dismutase (SOD), a glutamine residue (Q69) acting as a hydrogen bond donor to the inner sphere of the iron has been implicated in lowering the potential by -220 mV.^[11b] Conversely, increasing H-bond donation in the Fe-S protein rubredoxin has been shown to modulate the potential up to +126 mV.^[11a] A number of studies aimed at understanding how such hydrogen bonding influences metal complex reactivity and redox properties have also been published.^[12] In model complex work there is a much more obvious trend of second-sphere H-bonding interactions raising the redox potential of the metal as compared to the analogous complex with little to no second sphere interactions. Particularly relevant in the present context is recent work in which hydrogen bonding groups were introduced as unconstrained appendages in bis(carboxamido)pyridine ligands to evaluate their effects on redox potentials and/or catalytic activity of Cu(II) complexes.^[13] Herein, we evaluate the structures of a series of monocopper complexes of **H₂L4**²⁻ and the new purposefully mononucleating ligands **H₂L5**²⁻ (R' = H or *t*-Bu) in which the carboxamide N-H groups are held in place by the macrocycle. Different secondary sphere interactions were observed, and their role in influencing the redox properties of a subset of the compounds prepared was examined.

Results and Discussion

Complexes of **H₂L4**²⁻

The ligand precursor **H₄L4** was prepared using a modified version of published method.^[10] After initial attempts to generate dicopper complexes of **L4**⁴⁻ by treating **H₄L4** with excess base in the presence of Cu(II) salts (2 equiv) only yielded monocopper complexes **3–5**, a more purposeful synthesis was developed using 2 equiv of base and 1 equiv of CuX₂ (Scheme 1). The complexes were isolated as crystalline solids in modest yields, and characterized by electrospray ionization mass spectrometry (ESI-MS), EPR spectroscopy, CHN analysis, and X-ray crystallography (Figure 2). The X-ray structures reveal a common motif featuring a single Cu(II) ion bound to one bis(carboxamido)pyridyl portion of the macrocyclic ligand. The fourth chloride (**3**), acetate (**4**), and hydroxide (**5**) ligand is hydrogen bonded to two carboxamido N-H groups, as indicated by the appropriate NH-X and N...X distances (X = Cl, O-C(O)Me, OH; Table 1). For example, in **4**, O1...H4 = 2.202 Å, O1...H6 = 2.197 Å, O1...N4 = 3.003(2) Å, and O1...N6 = 3.002(2) Å. These parameters compare favorably to related ones reported previously for Cu(II) complexes of other carboxamido complexes.^[13] There is a slight elongation of the Cu-X (X = OH, Cl) distance

in **3** and **5** compared to analogous systems without hydrogen bonding, as in the case for **1b** vs. **5** where the Cu-OH distances are 1.863 Å and 1.884 Å respectively.^[8] Beyond the elongation of the Cu-X distances, the geometry around the Cu(II) center is nearly identical the non-hydrogen bonded systems. The retention of the indicated overall formulations for the complexes in solution was indicated by EPR spectroscopy (**3–5**) and negative ion mode ESI-MS (**3** and **4**; Figures S2-S4, Table S1); axial EPR signals and the appropriate parent ions and isotope patterns in the mass spectra are consistent with the respective monocopper species.

Similar performed on crystals selected randomly from the batch (Figures 3 and 4, Table 1). In both complexes, [(H₂L4)Cu] units surround a carbonate ion. In **6**, two such units are present, with the Cu(II)-O3 distance (2.5425(3) Å) longer than that for the equatorial O1 (1.9602(2) Å). This type of coordination mode has been seen in other examples of dicopper-carbonate complexes.^[14] Internal hydrogen bonding is evident between the macrocyclic N-H groups to the two O atoms of the carbonate that occupy the equatorial coordination positions (H4 and H6 to O1; H10 and H12 to O2), as reflected in the N-H...O distances (Table 1). The weak axial interaction Cu-O3 is broken in **7**, which features carbonate bound to three Cu(II) ions in η¹ fashion, a preceded tricopper-carbonate motif.^[15] Again, intramolecular hydrogen bonds between the macrocycle NH groups and the carbonate O atoms occurs, here resulting in complete sequestration of all of the available electron lone pairs of the carbonate ion in the complex.

In an effort to evaluate the effects on reactivity of the hydrogen bonding interactions in the complexes of **H₂L4²⁻**, we compared the cyclic voltammograms of the chloride and hydroxide complexes **3** and **5** to those of the previously reported^[8] complexes [(**L2**)CuX]⁻ (X = Cl or OH) that lack such interactions (Figure 5, Table 2). For the hydroxide complexes in DMF (Figure 5a, i and ii), a pseudo-reversible wave is seen for [(**L2**)CuOH]⁻ (*i*_{pc}/*i*_{pa} ~1, *E*_{1/2} = -67 mV vs. Fc⁺/Fc, *E*_p = 134 mV) similar to that which was reported previously in acetone or 1,2-difluorobenzene,^[8] but a return wave in the CV of **5** only becomes apparent at high scan rates, indicating high reactivity for the oxidized species. Importantly, the *E*_{1/2} for **5** is ~350 mV higher than that for [(**L2**)CuOH]⁻. Similarly, reversibility is greater for [(**L2**)CuCl]⁻ (Figure 5b) than for **3**, which shows only a small reverse scan wave at high scan rates, and the approximated *E*_{1/2} for **3** is ~300 mV higher than that for [(**L2**)CuCl]⁻. The significant redox potential increases for **3** and **5** relative to the complexes of **L2²⁻** are similar to ones reported previously for systems having analogous secondary-sphere motifs, for which it was proposed that the shifts were induced by removal of electron density from the metal center by the hydrogen bonding array.^[12] This rationale seems likely for our systems as well. However, the comparison between the systems supported by **H₂L4²⁻** and **L2²⁻** is complicated by the different nature of the carboxamide substituents (alkyl vs. aryl). To evaluate this influence and replicate the aryl substituents of [(**L2**)CuX]⁻ in a macrocyclic environment that would enable hydrogen bonding interactions but avoid the possibility of dinuclear complex formation that occurs with **L3⁴⁻**, we targeted complexes of ligand **H₂L5²⁻**.

Complexes of $\text{H}_2\text{L5}^{2-}$

Reported syntheses of macrocycle $\text{H}_4\text{L5}$ ($\text{R} = \text{H}$) and related macrocycles involve ring-closing condensations of a hemicycle precursor, N^2, N^6 -bis(2-aminophenyl)pyridine-2,6-dicarboxamide.¹⁶ Using a procedure similar to one previously described, $\text{H}_4\text{L5}$ was synthesized from the hemicycle via condensation with the corresponding isophthalic dichloride ($\text{R} = \text{H}$ or $t\text{-Bu}$; Scheme 2). Treatment of $\text{H}_4\text{L5}$ ($\text{R}' = \text{H}$ or $t\text{-Bu}$) with NMe_4OH (2 eq.) followed by CuX_2 ($\text{X} = \text{OAc}$ or Cl) yielded the monocopper complexes **8** ($\text{R}' = \text{H}$) and **9** ($\text{R}' = t\text{-Bu}$), respectively, the formulations of which were determined on the basis of EPR spectroscopy, high-resolution ESI-MS, and X-ray crystallography. Diagnostic axial signals in the EPR spectra and parent ions with the appropriate isotope patterns in the mass spectra were observed (Figures S6 and S7; Table S1). Interestingly, the X-ray crystal structures of these complexes revealed hydrogen bonding from the free carboxamide N-H groups to solvate molecules (**8**: DMF, the source of which is unclear; **9**: CH_3CN) instead of to the acetate or chloride ligands bound to the Cu(II) ion (Figure 6). The geometry around the Cu(II) center in **9** is nearly identical to that of $[(\text{L2})\text{CuCl}]^-$ with no elongation of the Cu-Cl distance as might be expected with no direct H-bond contact to the chloride. Importantly, the cyclic voltammogram of **9** contains a pseudo-reversible wave with $E_{1/2} = +581$ mV vs. Fc^+/Fc (Figure 5b, v) that is ~ 240 mV greater than that of $[(\text{L2})\text{CuCl}]^-$. Possible reasons for this difference include (a) attribution of the wave for **9** to a ligand-based redox process involving the aryl bridge instead of to a $\text{Cu}^{\text{II,III}}$ couple, (b) a difference between the electron donating properties of the carboxamide donors in the two complexes due to subtle differences between the aryl groups and/or their orientations, or (c) a change in the hydrogen bonding pattern in solution, resulting in N-H bonding to the chloride ligand as seen in the X-ray structures of **3–7**. Attempts to analyse these complexes in non hydrogen-bonding accepting solvent failed due to solubility issues of the analyte. Unfortunately, we are unable to distinguish unequivocally among these possibilities with the data currently available. Thus, returning to the question of the basis for the higher redox potentials observed for **3** and **5** relative to congeners supported by L2^{2-} , the difference between the carboxamide substituents remains a complicating factor. Nonetheless, we find it unlikely that the more electron donating alkyl carboxamides in **3** and **5** would cause an increase in the $\text{Cu}^{\text{II,III}}$ redox potential relative to aryl carboxamides in the complexes of L2^{2-} , and favor attribution of the observed $E_{1/2}$ differences to the effects of intramolecular hydrogen bonding.

Summary and Conclusions

Unlike macrocycle L3^{4-} , which forms dicopper complexes, treatment of $\text{H}_4\text{L4}$ with base and Cu(II) salts results in the formation of complexes in which $\text{H}_2\text{L4}^{2-}$ binds to a single Cu(II) ion. These complexes feature intramolecular hydrogen bonding between the carboxamide N-H groups to the fourth ligand (Cl , OAc , OH , or CO_3^{2-}) bound to the Cu(II) ion. These secondary coordination sphere hydrogen bonding interactions result in significant positive shifts in the $\text{Cu}^{\text{II/III}}$ redox potential, as shown by cyclic voltammetry experiments. We surmise that these shifts are not due to the ethyl linkers, as we observe a similar increase in the redox potential for the monocopper complex **9** supported by the purposefully mononucleating ligand $\text{H}_2\text{L5}^{2-}$ that features aryl groups on the carboxamido donors. While the X-ray structures of complexes of this ligand show a different hydrogen bonding pattern

involving interactions between the carboxamido groups and solvate molecules, we speculate that intramolecular hydrogen bonding in solution underlies the observed redox potential for **9**. Additional influences of the secondary sphere interactions in the various complexes we have prepared on their reactivity are the subject of continuing research.

Experimental Section

General

All reactions and manipulations were performed under an inert gas atmosphere using Schlenk techniques or a Glove box unless otherwise noted. HPLC grade Water was distilled and degassed by one freeze–pump–thaw cycle. The solvents tetrahydrofuran (THF), diethyl ether (Et₂O), pentane, dichloromethane (CH₂Cl₂) were passed through solvent purification columns (Glass Contour, Laguna, CA). Pyridine and ethylene diamine were purified by distillation prior to use. All chemicals were purchased from Aldrich and used without purification unless stated otherwise. Perpendicular-mode X-band (9.62 GHz) EPR spectra were recorded on a Bruker Elexsys E500 spectrometer. Simulations were performed using Bruker SimFonia software (version 1.25). Electrospray ionization mass spectrometry (ESI-MS) was performed on a Bruker Bio-TOF II instrument. Cyclic voltammetry (CV) was performed in a three electrode cell with Ag/Ag⁺ reference electrode, platinum auxiliary electrode, and platinum working electrode and analyzed with BASi Epsilon software. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) was used as the supporting electrolyte.

H₄L4

A procedure modified relative to that previously reported was used.^[12] This procedure was not performed using Schlenk line techniques. The compound **2**, 6-pyridine dicarboxylic acid (20 g, 0.120 mol) was dissolved in dry pyridine (250 mL) at 100 °C. To this homogeneous solution, stirred by a mechanical stirrer, was added a solution of ethylene diamine (6.5 mL, 0.120 mol) and pyridine (1 mL) dropwise from a syringe. A white solid formed and the mixture was stirred for 10 min. Triphenyl phosphite (63 mL, 0.240 mol) was then added to the reaction solution via an addition funnel and the mixture was stirred at 100 °C for an additional 5 h. The solution was then cooled to room temperature and stirred for an additional 12 h, after which the mixture was concentrated by removing the pyridine by distillation. The resulting white slurry was then washed with distilled water (2 × 50 mL), a 0.1 M solution of NaHCO₃ (2 × 200 mL), a 0.1 M solution of K₂CO₃ (2 × 200 mL), and 0.1 M solution of NaOH (2 × 200 mL). MeOH (40 mL) was added to the washed product and the mixture was refluxed for 40 min, cooled, and the solid collected via filtration using a Büchner funnel. After washing the white solid with additional MeOH (2 × 30 mL) and Et₂O (2 × 30 mL), it was allowed to dry in air. This white solid was then refluxed once more with 180 mL of DMF for 10 min, filtered while hot, and the filtrate allowed to cool to room temperature, producing white crystals of **H₄L4** (9.04 g, 40%). ¹H-NMR (DMSO-*d*₆, 300 MHz) δ (ppm): 9.46 (s, 4H, NHCO), 8.24–8.17 (m, 6H, CH^{Py}), 3.61–3.60 (m, 8H, CH₂). Anal. Calcd for C₁₈H₁₈N₆O₄: C, 56.54; H, 4.75; N, 21.98. Found: C, 56.67; H, 4.71; N, 21.97.

***N*-Boc-1, 2-phenylenediamine**

A procedure modified relative to that previously reported was used.^[16,17] This procedure was not performed using Schlenk line techniques. 1, 2-phenylenediamine (16.2 g, 0.150 mol) was added to 100% EtOH (300 mL) and the mixture was slowly heated to 30 °C until a clear yellow solution was obtained. A solution of Boc₂O (33.0 g, 0.150 mol) in EtOH (65 mL) was added dropwise over a 90 min period, keeping the temperature at 30 °C. After completing the addition the mixture was left to stir for 30 min, after which the volatiles were removed under vacuum to yield a white solid. To the raw product Et₂O (20 mL) and hexanes (20 mL) were added and a white solid was filtered off using Büchner funnel, washed with additional hexanes (20 mL), and the white crystalline product was dried in air. An additional amount of the product was obtained by slow evaporation of the filtrate over 2 d. The white crystals were collected by filtration, washed with hexane (2 × 10 mL), and dried in air (21.9 g, 70.4%). The ¹H NMR spectrum matched that which was reported.^[16,17] This compound was carried on as a precursor for the synthesis of the hemicycle, *N*²,*N*⁶-bis(2-aminophenyl)pyridine-2,6-dicarboxamide.

***N*²,*N*⁶-bis(2-aminophenyl)pyridine-2,6-dicarboxamide**

A procedure modified relative to that previously reported was used.¹⁰ Pyridine 2,6-dicarbonyl dichloride (5.0 g, 0.025 mol) was dissolved in dry THF (50 mL) and added dropwise to a solution of *N*-Boc-1,2-phenylenediamine (10.41 g, 0.050 mol) and NEt₃ in THF (300 mL) over 10 h. After the addition was complete, the mixture was stirred for 2 h and the resulting white solid was collected by filtration, washed with Et₂O (2 × 20 mL), and dried under vacuum. Next, the dried product was added to a mixture of CH₂Cl₂ (100 mL) and CF₃CO₂H (50 mL) and the mixture was stirred for 2 h. It was then carefully poured into aqueous NaOH (2M, 500 mL). The solution was immersed in an ice bath and allowed to cool. Additional CH₂Cl₂ (~900 mL) was added to dissolve all of the product, and the CH₂Cl₂ layer was washed with water (3 × 200 mL), dried over Na₂SO₄, and volatiles removed under vacuum to afford yellow solid. Recrystallization of this yellow solid from CH₂Cl₂ (100 mL) and Et₂O (100 mL) at 0 °C yielded pure compound **5** (8.68 g, 80%). ¹H-NMR matched reported values in literature.^[16,17]

H₄L5 (R' = H)

A procedure modified relative to that previously reported was used.¹⁷ A solution of isophthalic dichloride (1.18 g, 0.0058 mol) in dry THF (60 mL) was added dropwise over 12 h to a refluxing solution of **5** (2.0 g, 0.0058 mol) in a mixture of THF (250 mL) and NEt₃ (20 mL), all under Argon atmosphere. The mixture was cooled to room temperature, left to stir for an additional 24 h, filtered, and then solvent removed from the filtrate under vacuum to give a sticky brown solid. Addition of MeOH (300 mL) generated a white suspension that was filtered. The filtrate was collected and concentrated to ~50 mL and Et₂O (50 mL) was added to give a white powder that was collected by filtration and then washed with Et₂O (3 × 30 mL). The powder was redissolved in DMF (10 mL) and recrystallized with the addition of Et₂O (20 mL) at 0 °C over 24 hours to yield the product, which was dried under vacuum (0.94 g, 68%). ¹H-NMR (DMSO-*d*₆, 300 MHz) δ (ppm): 11.15 (s, 2H, NHCO), 10.21 (s, 2H, NHCO), 9.28 (s, 1H, CH), 8.43-8.40 (d, 2H, CH^{Py}), 8.29-8.24 (m, 1H, CH^{Py}), 8.15-8.07

(m, 4H, CH), 7.72-7.66 (m, 2H, CH), 7.37-7.25 (m, 4H, CH). Anal Calcd for $C_{30}H_{26}N_6O_5$ (**H₄L5** (**R'**=**H**) with one molecule of DMF) C, 65.45; H, 4.76; N, 15.26. Found: C, 64.57; H, 4.70; N, 15.32.

H₄L5 (**R'** = ***t*-Bu**)

This compound was synthesized analogously to **H₄L5** (**R'** = **H**) except 5-*tert*-butyl-isophthalic dichloride was used instead of isophthalic dichloride (1.85 g, 60.2%). ¹H-NMR (DMSO-*d*₆, 300 MHz) δ (ppm): 11.25 (s, 2H, NHCO), 10.30 (s, 2H, NHCO), 9.22 (s, 1H, CH), 8.42-8.39 (d, 2H, CH^{Py}), 8.28-8.22 (m, 1H, CH^{Py}), 8.10-8.04 (m, 4H, CH), 7.68-7.65 (m, 2H, CH), 7.36-7.26 (m, 4H, CH), 1.33 (s, 9H, CH₃). Calcd for $C_{34}H_{34}N_6O_5$ (**H₄L5** (**R'** = ***t*-Bu**) with one molecule of DMF): C, 67.31; H, 5.65; N, 13.85. Found: C, 67.02; H, 6.01; N, 13.80.

[NMe₄][(H₂L4)Cu(Cl)] (**3**)

To a solution of **H₄L4** (300 mg, 0.78 mmol) in 1:3 water (3 mL)/pyridine (9 mL) was added a solution of NMe₄OH in MeOH (0.38 mL, 0.0017 mol, 2.18 M). Upon addition of base and with vigorous stirring, a clear, yellow solution resulted. An equivalent of CuCl₂ (105 mg, 0.78 mmol) was added slowly to the yellow solution, which gradually turned green and eventually purple upon stirring. After allowing to stir for 12 h, the solvent was removed under vacuum and the resulting purple powder was dissolved in DMF (5 mL). Vapor diffusion of Et₂O into the solution afforded the product as purple crystals which were dried under vacuum (0.236 g, 58%). HR-MS (ESI-, CH₃OH): m/z = 478.137. Calc. for [**3** - NMe₄⁺]⁻: 478.022. Anal. Calcd for C₂₂H₂₈ClCuN₇O₄: C, 47.74; H, 5.10; N, 17.71. Found: C, 47.79; H, 5.14; N, 17.24.

[NMe₄][(H₂L4)Cu(OAc)] (**4**)

Compound **4** was prepared analogously to **3** except Cu(OAc)₂·H₂O was used instead of CuCl₂ (0.187 g, 42%). HR-MS (ESI-, CH₃OH): m/z = 502.032. Calc for [**4** - NMe₄⁺]⁻: 502.066. Anal. Calcd for C₂₄H₃₁CuN₇O₆: C, 49.95; H, 5.41; N, 16.99. Found: C, 49.26; H, 5.59; N, 16.74.

[NMe₄][(H₂L4)Cu(OH)] (**5**)

The compound **H₄L4** (300 mg, 0.78 mmol) was added to a degassed solution of 1:3 water/pyridine. Subsequently, 0.55 mL (0.0025 mol) of a 2.18 M NMe₄OH solution in water was added to this solution resulting in a yellow color. An equivalent of Cu(OTf)₂ (281 mg, 0.78 mmol) was added slowly to the solution resulting in a slight green color that turned purple after stirring for several minutes. The solution was left to stir for 12 hours and then the solvent was removed under high vacuum. The resulting purple powder was dissolved in DMF (10 mL) and an equivalent amount of Et₂O (10 mL) was added and placed in a vial and left to sit under Nitrogen atmosphere at room temperature. After 5 days purple crystals were observed on the sides of the vial that were found to be **5** (53 mg, 12%). Anal Calcd for C₂₂H₂₉CuN₇O₅: C, 49.39; H, 5.46; N, 18.32. Found: C, 49.05; H, 5.93; N, 17.97.

(NMe₄)₂[(H₂L4Cu)₂CO₃] (6) and (NMe₄)₂[(H₂L4Cu)₃CO₃] (7)

Compound **5** (200mg, 0.40 mmol) was dissolved in 10 mL of DMF was left open to atmospheric CO₂ for over 24 hours. Upon Et₂O vapor diffusion into the DMF solution, purple crystals were isolated and identified as a mixture of **6** and **7** by X-ray crystal structures of randomly selected crystals. An ESI-mass spectrum of one crystal was consistent with **7** (ESI-, CH₃OH): *m/z* = 695.754. Calc for [**7** - 2 NMe₄⁺]²⁻: 695.571. Because the product was identified as a mixture, no CHN analysis was attempted.

NMe₄[(H₂L5)CuCl] (9, R' = *t*-Bu)

To a solution of ligand **H4L5** (R' = *t*-Bu) (200 mg, 0.3 mmol) in dry MeCN, 0.13 mL (0.6 mmol) of a 2.18 M NMe₄OH solution in MeOH was added and the solution was left to stir for 10 min. resulting in a clear yellow solution. To this yellow solution an equivalent of dry CuCl₂ (40 mg, 0.3 mmol) was added resulting in a green color change of the solution. The reaction was left to stir at room temp for 2 hours and the solution was filtered and solvent removed to afford a green powder. The powder was dissolved in acetone (10 mL), filtered, and the solvent removed to afford **9** (140 mg, 66%). Crystals of **9** were obtained by slow evaporation of Et₂O into a concentrated solution of **9** in dry MeCN. HR-MS (ESI-, CH₃OH): *m/z* = 631.134. Calc for [**9** - NMe₄⁺]⁻: 630.568. Repeated attempts to obtain correct CHN analysis were unsuccessful, which we attribute to incomplete combustion.

NMe₄[(H₂L5)CuOAc] (8)

Compound **8** was prepared analogously to **9** except Cu(OAc)₂·H₂O was used instead of CuCl₂ (125 mg, 62%). Crystals of **8** were obtained by slow evaporation of Et₂O into a concentrated solution of **8** in dry DMA. HR-MS (ESI-, CH₃OH): *m/z* = 597.136. Calc. for [**8** - NMe₄⁺]⁻: 597.071. Repeated attempts to obtain correct CHN analysis were unsuccessful, which we attribute to incomplete combustion.

X-ray crystallography

All crystals were placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker APEX II Platform CCD diffractometer or a Bruker D8 Photon 100 CMOS diffractometer for data collection. The data collections were carried out using MoKα or CuKα radiation with a graphite monochromator (λ = 0.71073 Å or 1.54184 Å) at 173 K or 123 K respectively. Structure solutions were performed by direct methods using SHELXS-2013 software^[18] and refined against F₂ using full-matrix-least-squares using SHELXL-97^[19] and SHELXL-2013 software.^[18] All hydrogen atoms were placed as idealized and refined in a riding approximation. The thermal ellipsoids of the hydrogen atoms were bonded to the parent atom as follows: U_{iso}(H) = 1.2U_{eq}(N/C) for aromatic, amide, and -CH₂- protons and U_{iso}(H) = 1.5U_{eq}(N/C) for -CH₃ protons, where U_{eq} = 1/3(U₁₁ + U₂₂ + U₃₃). The structure for **9** was found to be a non-merohedral twin, in which two twin components are related to each other by a rotation around the a* direction in reciprocal space. The corresponding twin law was found to be 1 0 0 0 -1 0 1 0 -1. The CCDC codes for the deposited data are as follows: 1424005 (**7**); 1424006 (**6**); 1424007 (**3**); 1424008 (**4**); 1424009 (**5**); 1424010 (**8**); 1424011 (**9**).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank the NIH (GM47365) and DARPA for financial support, and Dr. Victor G. Young, Jr., for assistance with X-ray crystallography, which was performed using a crystal diffractometer acquired through NSF-MRI Award CHE-1229400.

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Figure 1.
Ligands and complexes discussed herein.

Figure 2.

Representations of the anionic portions of the X-ray structures of (a) $[\text{NMe}_4][\text{H}_2\text{L4Cu}(\text{Cl})]$ (**3**), (b) $[\text{NMe}_4][\text{H}_2\text{L4Cu}(\text{OAc})]$ (**4**), and (c) $[\text{NMe}_4][\text{H}_2\text{L4Cu}(\text{OH})]$ (**5**), showing all nonhydrogen atoms as 50% thermal ellipsoids and hypothesized hydrogen bonds as dashed lines.

Figure 3.

(a) Representation of the anionic portion of the X-ray structure of [NMe₄]₂[((H₂L4)Cu)₂(CO₃)] (6), showing all nonhydrogen atoms as 50% thermal ellipsoids and hypothesized hydrogen bonds as dashed lines. (b) Expanded view of core, with all carbon atoms (except C36) omitted.

Figure 4.

(a) Representation of the anionic portion of the X-ray structure of $[\text{NMe}_4]_2[(\text{H}_2\text{L4})\text{Cu}_3(\text{CO}_3)]$ (7), showing all nonhydrogen atoms as 50% thermal ellipsoids and hypothesized hydrogen bonds as dashed lines. (b) Expanded view of core, with all carbon atoms (except C63) omitted.

Figure 5.

Cyclic voltammograms (0.1 M Bu_4NPF_6 , Pt electrode) of (a) the complexes (i) $[(\text{L}2)\text{CuOH}]^-$ and (ii) $[(\text{H}_2\text{L}4)\text{CuOH}]^-$ (**5**) in DMA, and (b) the complexes (iii) $[(\text{L}2)\text{CuCl}]^-$, (iv) $[(\text{H}_2\text{L}4)\text{CuCl}]^-$ (**3**), and (v) $[(\text{H}_2\text{L}5)\text{CuCl}]^-$ (**9**, $\text{R}' = t\text{-Bu}$) in CH_3CN . Scan rates: (i) 500 mV s^{-1} , (ii) 500 (black), 2000 (blue), 4000 (red) mV s^{-1} , (iii) 100 mV s^{-1} , (iv, v) 500 (black), 2000 (blue), 4000 (red) mV s^{-1} .

Figure 6.

(a) Representations of the anionic portion of the X-ray structures of (a) $[\text{NMe}_4][(\text{H}_2\text{L5})\text{Cu}(\text{OAc})] \cdot \text{DMF}$ (**8**, $\text{R}' = \text{H}$) and (b) $[\text{NMe}_4][(\text{H}_2\text{L5})\text{CuCl}] \cdot \text{CH}_3\text{CN}$ (**9**, $\text{R}' = t\text{-Bu}$), showing all nonhydrogen atoms as 50% thermal ellipsoids and hypothesized hydrogen bonds as dashed lines.

Scheme 1.

Synthesis of complexes of **H₂L₄²⁻**. (i) NMe₄OH (2 eq.), CuX₂ (X = Cl, OAc, or OTf). (ii) air, DMF.

Scheme 2.

Synthesis of **H₄L5** and complexes **8** and **9**. (i) NEt_3 , THF. (ii) (a) CF_3CO_2H (b) $NaOH$ (c) isophthalic or 5-*tert*-butyl isophthalic dichloride, NEt_3 , THF. (iii) NMe_4OH (2 eq.), CuX_2 ($X = Cl$ or OAc), S .

Table 1
Selected Interatomic Distances (Å) and Angles (deg) for the Indicated X-ray Crystal Structures

[NMe ₄][H ₂ L4Cu(Cl)] (3)		
Cu1 – N1	1.986(2)	N4...Cl1 3.393(3)
Cu1 – N2	1.926(2)	N6...Cl1 3.390(2)
Cu1 – N3	1.984(2)	H4...Cl1 2.602
Cu1 – Cl1	2.2408(8)	H6...Cl1 2.628
		N2 – Cu1 – N3 80.78(10)
		Cl1 – Cu1 – N3 98.77(7)
		N1 – Cu1 – N3 161.01(10)
[NMe ₄][H ₂ L4Cu(OAc)] (4)		
Cu1 – N1	1.980(2)	N4...O1 3.003(2)
Cu1 – N2	1.920(2)	N6...O1 3.002(2)
Cu1 – N3	1.991(2)	H4...O1 2.202
Cu1 – O1	1.937(1)	H6...O1 2.197
Cu1 – O2	2.636(2)	
		N2 – Cu1 – O1 171.46(6)
		N2 – Cu1 – N1 80.97(7)
		O1 – Cu1 – N1 99.43(6)
		N2 – Cu1 – N3 80.73(7)
		O1 – Cu1 – N3 98.11(6)
		N1 – Cu1 – N3 161.31(7)
[NMe ₄][H ₂ L4Cu(OH)] (5)		
Cu1 – N1	2.005(2)	N4...O1 2.890(2)
Cu1 – N2	1.931(2)	N6...O1 2.865(2)
Cu1 – N3	2.002(2)	H4...O1 2.038
Cu1 – O1	1.884(1)	H6...O1 2.055
		N2 – Cu1 – O1 172.85(7)
		N2 – Cu1 – N1 80.08(7)
		O1 – Cu1 – N1 99.69(6)
		N2 – Cu1 – N3 80.27(7)
		O1 – Cu1 – N3 99.59(7)
		N1 – Cu1 – N3 160.25(7)
[NMe ₄] ₂ [(H ₂ L4)Cu ₂ (CO ₃)] (6)		
Cu1 – N1	1.982(2)	N4...O1 2.957(4)
Cu1 – N2	1.931(2)	N6...O1 3.024(4)
Cu1 – N3	1.982(2)	H4...O1 2.106
Cu1 – O1	1.960(2)	H6...O1 2.170
		N2 – Cu1 – O1 169.46(8)
		N2 – Cu1 – N1 80.38(9)
		O1 – Cu1 – N1 99.96(8)
		N2 – Cu1 – N3 80.32(9)

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Cu1 – O3	2.543(3)	N10...O2	3.1939(48)	O1 – Cu1 – N3	98.30(8)
Cu2 – N7	1.991(2)	N12...O2	3.1276(50)	N1 – Cu1 – N3	160.32(9)
Cu2 – N8	1.919(2)	H10...O2	2.019	N8 – Cu2 – O2	177.96(9)
Cu2 – N9	2.019(3)	H12...O2	1.908	N8 – Cu2 – N7	80.84(10)
Cu2 – O2	1.908(2)			O2 – Cu2 – N7	99.76(10)
				N8 – Cu2 – N9	80.50(10)
				O2 – Cu2 – N9	98.68(10)
				N7 – Cu2 – N9	160.35(10)

[NMe ₄] ₂ [(H ₂ L ₄)Cu ₃ (CO ₃)] (7)					
Cu1 – N1	1.979(3)	N4...O1	3.045(4)	N2 – Cu1 – O1	171.37(12)
Cu1 – N2	1.923(3)	N6...O1	3.167(4)	N2 – Cu1 – N1	80.68(14)
Cu1 – N3	1.991(3)	H4...O1	2.219	O1 – Cu1 – N1	100.31(12)
Cu1 – O1	1.945(3)	H6...O1	2.395	N2 – Cu1 – N3	80.35(14)
Cu2 – N7	1.979(3)	N10...O2	3.108(4)	O1 – Cu1 – N3	97.95(12)
Cu2 – N8	1.919(3)	N12...O2	3.140(4)	N1 – Cu1 – N3	160.75(14)
Cu2 – N9	1.975(3)	H10...O2	2.440	N8 – Cu2 – O2	168.19(12)
Cu2 – O2	1.949(3)	H12...O2	2.421	N8 – Cu2 – N7	80.36(13)
Cu3 – N13	1.987(4)	N16...O3	3.090(5)	O2 – Cu2 – N7	99.71(12)
Cu3 – N14	1.931(3)	N18...O3	2.984(4)	N8 – Cu2 – N9	80.87(13)
Cu3 – N15	1.977(4)	H16...O3	2.503	O2 – Cu2 – N9	98.46(12)
Cu3 – O3	1.942(3)	H18...O3	2.398	N7 – Cu2 – N9	161.21(13)
				N14 – Cu3 – O3	173.86(13)
				N14 – Cu3 – N13	80.08(16)
				O3 – Cu3 – N13	98.16(13)
				N14 – Cu3 – N15	81.17(16)
				O3 – Cu3 – N15	99.94(13)
				N13 – Cu3 – N15	160.54(14)

[NMe ₄][(H ₂ L ₅)Cu(OAc)] • DMF (8, R' = H)					
Cu1 – N1	2.005(2)	N4...O7	3.096(5)	N2 – Cu1 – O1	177.84(6)
Cu1 – N2	1.915(2)	N5...O7	3.164(3)	N2 – Cu1 – N1	80.55(6)

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Cu1 – N3	2.018(2)	H4...O7	2.183	O1 – Cu1 – N1	100.68(6)
Cu1 – O1	1.912(1)	H5...O7	2.691	N2 – Cu1 – N3	81.00(7)
Cu1 – O2	2.819(2)			O1 – Cu1 – N3	97.65(6)
				N1 – Cu1 – N3	161.14(7)
[NMe ₄][(H ₂ L5)(CuCl)] • CH ₃ CN (9 , R' = <i>i</i> Bu)					
Cu1 – N1	2.043(2)	N4...N6	3.348(3)	N2 – Cu1 – Cl1	178.05(5)
Cu1 – N2	1.918(2)	N5...N6	4.013(3)	N2 – Cu1 – N1	80.56(7)
Cu1 – N3	2.021(2)	H4...N6	2.602	Cl1 – Cu1 – N1	99.81(5)
Cu1 – Cl1	2.1852(5)	H5...N6	2.628	N2 – Cu1 – N3	80.23(6)
				Cl1 – Cu1 – N3	99.62(5)
				N1 – Cu1 – N3	159.62(7)

Table 2Redox potentials for the indicated copper complexes.^a

Compound	Solvent	E _{1/2} (mV)
[(L2)CuOH] [−]	DMA	−67
[(H₂L4)CuOH] [−] (5)	DMA	+284
[(L2)CuCl]	CH ₃ CN	+338
[(H₂L4)CuCl] [−] (3)	CH ₃ CN	+632
[(H₂L5)CuCl] [−] (9)	CH ₃ CN	+581

^a Conditions: room temperature, 0.1 M Bu₄NPF₆, Pt electrode.^b vs. Fc⁺/Fc.