Published in final edited form as:

Inorganica Chim Acta. 2019 January 24; 485: 131–139. doi:10.1016/j.ica.2018.10.011.

Copper Complexes of Multidentate Carboxamide Ligands

Courtney E. Elwell[†], Benjamin D. Neisen[†], and William B. Tolman^{§,*}

[†] Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455

[§] Department of Chemistry, Washington University in St. Louis, Campus Box 1134, 1 Brookings Drive, St. Louis, MO 63130.

Abstract

The copper coordination chemistry of two multidentate carboxamido ligands derived from HL¹ (offering two quinolyl and one carboxamide donor) and H₄L² (with two pyridine(dicarboxamido) units linked by naphthalene spacers) was explored. The former was chosen because upon deprotonation it would provide a monoanionic *mer*-coordinating N-donor set that would model the putative deprotonated form of the His-brace in copper monooxygenases, while the latter was designed to bind two copper ions and enable comparisons to other systems with different ligand spacers. Upon reaction with Cu(I)-mesityl, HL¹ yielded a symmetric dimer (**L¹Cu**)₂ in which each bis(quinolyl)amide ligand binds via two N-donors to one Cu(I) ion and via the third to the other Cu(I) center. Monomeric Cu(II) complexes [**L¹Cu(H₂O**)₂](OTf) and **L¹₂Cu** were also characterized. Treatment of H₄L² with Cu(OTf)₂ and excess Me₄NOH (in CH₃CN, pyridine/H₂O, or MeOH) yielded complexes with anions of general formula [**L²Cu₂(X)**]ⁿ⁻, where X = CH₃CONH⁻ (n = 1), CO₃²⁻ (n = 2), or MeO⁻ (n = 1). X-ray structures of these complexes revealed the (L²)⁴⁻ ligand binding to two Cu(II) ions in an open paddle-wheel geometry, with an additional bridging ligand (X) completing the square planar coordination sphere of each metal ion. The open paddlewheel motif differs from the more ‘open’ puckered geometry seen with related ligands with different spacer units.

Graphical Abstract:

*Corresponding author: wbtolman@wustl.edu.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Keywords

copper; ligand synthesis; carboxamide

1. Introduction.

As part of multidisciplinary efforts to understand the mechanisms of action of oxidases and oxygenases comprising copper active sites [1], oxidized copper complexes relevant to proposed reaction intermediates have been chosen for study [2]. Carboxamide ligands have been found to be useful in such studies because of their strong electron donating properties that stabilize metals in high oxidation states [3]. Notable in this context has been the isolation of a variety of formally Cu(III) complexes using tetradentate dicarboxamide ligands [4]. In previous work from our laboratory focused primarily on pyridine(2,6-dicarboxamides) [5], the ligand precursors shown in Figure 1 were used to prepare models of putative copper-oxygen enzyme intermediates [6,7], including ones with [Cu(OH)]²⁺ [6] and mixed-valent [Cu₂(OH)]⁴⁺ cores [7c] comprising formally Cu(III) sites. In an extension of this research, we targeted ligand precursors HL¹ [8] and H₄L² (Figure 1) because we hypothesized that they would have advantageous features relative to **A-E**. We selected HL¹ because upon deprotonation it would provide a monoanionic *mer*-coordinating N-donor set (complementary to **A** and **B**) that would model the putative deprotonated form of the His/His-brace in lytic polysaccharide monooxygenase and methane monooxygenase [9]. We chose H₄L² in order to explore how changing the nature of the bridging unit between pyridine(dicarboxamide) donors (relative to those in **C** and **D**) would influence the structures and properties of dicopper cores relevant to catalytic oxidations. Herein, we describe the syntheses of these two ligand precursors and the results of preliminary explorations of the copper coordination chemistry of their deprotonated variants, including the discovery of several unexpected structural motifs.

2. Materials and Methods

Preparation and handling of the air-sensitive compounds were carried out under a dinitrogen atmosphere either in a glove-box or using Schlenk techniques. All reagents and solvents

were purchased from commercial sources and used as received unless otherwise noted. Tetrahydrofuran (THF) was dried over sodium/benzophenone and vacuum distilled. Chloroform (CHCl_3) and dichloromethane (CH_2Cl_2) were dried over CaH_2 and vacuum distilled. Diethyl ether (Et_2O) was passed through a solvent purification column (Glass Contour, Laguna, CA). All anhydrous solvents were stored over 3 Å molecular sieves in a N_2 filled glove-box prior to use. HPLC grade ethyl acetate (EtOAc), 200 proof ethanol (EtOH) and water were used without further purification. HPLC grade water was distilled and degassed. Pyridine was purified by distillation prior to use. Anhydrous benzene, benzotriazole (99%), quinaldic acid (98%), trimethylamine (99%), aqueous ammonium hydroxide (30%), potassium hydride (97%), 2-quinaldoyl chloride (97%), and triethylammonium hydroxide solution in water (1.40 M) were purchased from SigmaAldrich and used without further purification unless otherwise noted. Anhydrous copper(II) trifluoromethanesulfonate (98%) was purchased from Strem Chemicals and used without further purification. The compounds *N*-(1-methanesulfonyl)benzotriazole [10] and copper(I) mesityl [11] were synthesized via previously published procedures.

For X-ray crystallography experiments, crystals were placed onto the tip of a 0.1 mm diameter glass capillary or mitogen polymer tip 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 $\text{MoK}\alpha$ or $\text{CuK}\alpha$ radiation with a graphite monochromator ($\lambda = 0.71073 \text{ \AA}$ or $1.54184 \text{ \AA}$) at 173 K or 123 K respectively. Structure solutions were performed by direct methods using SHELXS-2013 software and refined against F^2 using full-matrix-leastsquares using SHELXL-97 and SHELXL-2013 software. [12]

3. Experimental

2-quinolinyl(acylbenzotriazole) (1).

The following procedure was scaled up from a previously reported synthesis of 2-quinolinyl(acylbenzotriazole) [13]. Quinaldic acid (4.53 g, 26.2 mmol) and 1-(methanesulfonyl)benzotriazole (5.16 g, 26.2 mmol) were fully dissolved in 130 mL THF, resulting in a colorless solution. Triethylamine (5.12 mL, 36.7 mmol) was added dropwise to the THF solution, resulting in a cloudy white mixture, and refluxed overnight. After several hours, the solution turned deep red/pink. Upon, cooling the solvent was then removed *in vacuo* and the resulting red solid was redissolved in 260 mL CHCl_3 . The orange/red solution was then washed once with deionized water and then 3 M brine ($3 \times 200 \text{ mL}$), the organic layer was dried over anhydrous Na_2SO_4 , and CHCl_3 was evaporated to yield an orange solid. This solid was recrystallized via dissolution into a small amount of near boiling CHCl_3 (25 mL), addition of 30 mL hexanes, and storage in a -20°C freezer overnight, to yield a pink fluffy solid. The solid was isolated via vacuum filtration and dried for 6 h in a vacuum oven (3.96 g, 55% yield). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.43 (dd, $J = 8.6, 2.0 \text{ Hz}$, 2H), 8.27 (d, $J = 8.5 \text{ Hz}$, 1H), 8.20 (dt, $J = 8.3, 0.8 \text{ Hz}$, 1H), 8.10 (d, $J = 8.5 \text{ Hz}$, 1H), 7.96 (dd, $J = 8.3, 1.5 \text{ Hz}$, 1H), 7.84 (ddd, $J = 8.5, 6.8, 1.5 \text{ Hz}$, 1H), 7.74 (m, 2H), 7.59 (m, 1H). The ^1H NMR spectrum matched that previously published so the product was used without further purification.

2-quinolinecarboxamide.

The following procedure was adapted from a previously reported synthesis for 2-pyridinecarboxamide [10]. Other synthetic procedures have been reported for 2-quinolinecarboxamide [14], yet, this new procedure was used to avoid hazardous and/or expensive reagents without sacrificing yield. To a 250 mL round bottom flask, 2quinoliny(acylbenzotriazole) (3.00 g, 11 mmol) was dissolved in 22 mL of 200 proof EtOH and 22 mL THF to yield a light pink solution. To this solution was added 22 mL (341 mmol) of ammonium hydroxide (30% aqueous solution) dropwise, resulting in a clear light orange-yellow solution. The solution was allowed to stir for 4 h at room temperature. The solvents were then removed *in vacuo* with gradual heating up to 40 °C to provide a fluffy white solid. The solid was then suspended in 60 mL of 2 M NaOH and allowed to stir for 10 min. To the suspension, 60 mL EtOAc was added and allowed to stir vigorously for an additional 10 min. The mixture was transferred to a 1 L separation funnel, shaken vigorously and the aqueous layer removed. The organic layer was washed once more with 60 mL of 2 M NaOH (NOTE: heat released, so careful venting needed). The organic layer was washed with saturated brine (2 × 60 mL) and dried over Na₂SO₄. The EtOAc was removed *in vacuo* to yield a fluffy white solid that appeared pure by ¹H NMR spectroscopy (1.21 g, 65% yield). The isolated solid was utilized without further purification. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.31 (s, 2H), 8.11 (d, *J* = 0.7 Hz, 1H), 8.09 (bs, 1H), 7.87 (ddd, *J* = 8.2, 1.5, 0.7 Hz, 1H), 7.76 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.62 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 6.11 (bs, 1H). ¹³C NMR (400 MHz, CDCl₃) δ (ppm): 167.2, 149.5, 146.7, 137.6, 130.2, 130.0, 129.5, 128.2, 127.8, 118.9. Comparison of the product NMR spectra with those previously published confirmed that the desired product was made.

Potassium 2-quinolinecarboxamido (2).

Safety Note: This reaction produces highly flammable H₂ gas and should be completed in a reaction vessel that can tolerate pressures above 1 atm. It is recommended that a simple calculation be done prior to scaling up this reaction to minimize pressure buildup. In a 50 mL Schlenk flask in a N₂-filled glove-box, 2quinolinecarboxamide (0.377 g, 2.19 mmol) was dissolved in 8 mL dry THF, resulting in a clear, off-white solution. A suspension of KH (0.0879 g, 2.19 mmol) in 8 mL dry THF was added dropwise to the 2-quinolinecarboxamide solution. After approximately 2 h, a white solid began to precipitate out of the THF. The reaction was stirred overnight (~12 h) and the white precipitate was isolated via vacuum filtration using a fine, 2 mL frit in the N₂-filled glovebox. The solid was washed with ~ 20 mL pentane and used without further purification (0.436 g, 95% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 8.20 (m, 2H, CH), 8.02 (d, *J* = 0.8 Hz, 1H, CH), 7.91 (d, *J* = 0.7 Hz, 1H, CH), 7.70 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H, CH), 7.53 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H, CH). ¹³C NMR (400 MHz, DMSO-*d*₆) δ (ppm): 170.8, 146.5, 132.3, 129.2, 128.8, 127.5, 127.3, 125.8, 120.3. HR-MS (ESI, DMA/MeOH) *m/z*: [K₂(2-quinolinecarboxamido)]⁺ Calcd. for [C₁₀H₇N₂OK₂]⁺ 248.9866; found 248.9838 (Figures S1 – S3). Anal. Calc. for C₁₀H₇KN₂O: C, 57.12; H, 3.36; N, 13.32. Found: C, 56.53; H, 3.59; N, 13.12.

HL¹.

To a dry 100 mL Schlenk flask in a N₂-filled glove-box, potassium 2quinolinecarboxamido (300 mg, 1.45 mmol) and 2-quinaldoyl chloride (277 mg, 1.46 mmol) were added as solids. The Schlenk flask was then taken out of the glove-box to be used on the Schlenk line and 50 mL of anhydrous benzene were added via cannula transfer. The resultant purple mixture was refluxed at 80 °C under Ar overnight, resulting in a magenta colored solution. After cooling to room temperature, a dark purple solid precipitated. The solid was isolated via vacuum filtration and found to be > 90 % pure via ¹H NMR spectroscopy. Further purification was achieved via recrystallization in a minimal amount of near-boiling benzene followed by immediate cooling in a 10 °C ice/water bath to yield the product as an off-white solid (240 mg, 51% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 13.68 (s, 1H, NH), 8.42 (m, 6H, CH), 7.97 (d, *J* = 8.2 Hz, 2H, CH), 7.91 (m, 2H, CH), 7.73 (dd, *J* = 8.3, 6.7 Hz, 2H, CH). ¹³C NMR (400 MHz, CDCl₃) δ (ppm): 162.9, 149.0, 146.6, 138.1, 130.7, 130.5, 130.1, 129.0, 128.0, 119.3. HR-MS (ESI, MeOH) *m/z*: [HL¹ + Na]⁺ Calcd. for [C₂₀H₁₃N₃O₂Na]⁺ 350.0905; found 350.0267. Anal. Calc. for C₂₀H₁₃N₃O₂: C, 73.38; H, 4.00; N, 12.80. Found: C, 72.59; H, 3.76; N, 12.64. The spectroscopic and elemental analysis data were consistent with what was previously published for HL¹ [8] and thus the product was used without further purification.

[L¹Cu(H₂O)₂](OTf).

In a 20 mL vial with heating, anhydrous copper(II) trifluoromethanesulfonate (221 mg, 0.61 mmol) was dissolved in 15 mL of 90% EtOH. After cooling to room temperature, HL¹ (200 mg, 0.61 mmol) was added to the pale blue solution, which became blue-green. The mixture was heated to boiling to ensure all reactants were dissolved, and then cooled to room temperature, at which point the solution was green-blue and contained a teal precipitate. The precipitate was isolated via gravity filtration as a bright teal powder (256 mg, 71%). HR-MS (ESI, MeOH) *m/z*: [L¹Cu]⁺ Calcd. for [CuC₂₀H₁₂N₃O₂]⁺ 389.0226; found 388.9763; *m/z* [L¹Cu^{II}(EtOH)]⁺ Calcd. for [CuC₃₂H₁₈N₃O₃]⁺ 435.0644; found 435.0132 (Figure S4). Anal. Calc. for CuC₂₁H₁₄N₃O₆SF₃: C, 45.29; H, 2.53; N, 7.54. Found: C, 45.06; H, 2.74; N, 8.09. X-ray quality crystals in the form of teal blocks were grown upon slow diffusion of anhydrous THF into a concentrated solution of the compound in EtOH at room temperature.

(L¹Cu)₂.

In a 20 mL vial in a N₂-filled glove-box, HL¹ (50 mg, 0.15 mmol) was suspended in 2 mL of dry THF, resulting in a pale pink mixture. In a separate 20 mL vial, copper(I) mesityl (29 mg, 0.16 mmol) was dissolved in 1 mL of dry THF, resulting in a bright yellow-orange solution. The copper(I) mesityl was added dropwise to the suspension of HL¹ in THF, which transitioned from pale pink to hot pink to dark brown. After stirring for 1 h, a dark red-brown precipitate formed and was isolated via vacuum filtration (32 mg, 53% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 8.23 (d, *J* = 8.4 Hz, 2H, CH), 8.17 (d, *J* = 8.5 Hz, 2H, CH), 7.97 (dd, *J* = 8.2, 1.5 Hz, 2H, CH), 7.81 (ddd, *J* = 8.5, 6.8, 1.6 Hz, 2H, CH), 7.75 (m, 2H, CH), 7.31 (d, *J* = 8.5 Hz, 2H, CH). ¹³C NMR (400 MHz, DMSO-*d*₆) δ (ppm): 170.7, 152.7, 143.2, 137.8, 131.2, 129.2, 129.0, 128.6, 127.9, 119.5 (Figures S5 – S7). UV-vis (CH₂Cl₂, –80 °C) λ_{max}, nm (ε, M^{–1} cm^{–1}): 465 (2800), 510 (3000). Anal. Calc. for

$\text{Cu}_2\text{C}_{44}\text{H}_{32}\text{N}_6\text{O}_5$: C, 62.04; H, 3.79; N, 9.87. Found: C, 62.13; H, 4.15; N, 9.49. X-Ray quality crystals in the form of dark red-brown needles were grown upon slow diffusion of anhydrous THF into a concentrated solution of the complex in CH_2Cl_2 at room temperature.

$>\text{L}^1_2\text{Cu}$.

In a 20 mL vial within a N_2 -filled glovebox, $(\text{L}^1\text{Cu})_2$ (41.1 mg, 0.053 mmol) was dissolved in 13 mL of anhydrous CH_2Cl_2 to afford a red-brown solution. The vial was capped, brought out of the glovebox and opened to air. After 24 h, the solution had turned green. The solvent was removed *in vacuo*, resulting in a green fine powder (25.1 mg, 66% yield). HR-MS (ESI, DMF/MeOH) *m/z*: $[\text{L}^1\text{CuCl}_2]^-$ Calcd. for $[\text{CuC}_{20}\text{H}_{12}\text{N}_3\text{O}_2\text{Cl}_2]^-$ 458.9585; found 458.9152 (Figures S7 – S8). X-Ray quality crystals in the form of light green (highly symmetric) square bipyramids were obtained upon slow evaporation of a concentrated solution of $(\text{L}^1\text{Cu})_2$ in CH_2Cl_2 in air at room temperature. Despite repeated attempts, we were unable to obtain accurate and reproducible CHN analysis.

H_4L^2 .

To a flask containing 150 mL dry THF was added 2,6-pyridinedicarbonyl dichloride (4.0 g, 0.02 mol) and 20 mL (0.12 mol) *N,N*-diisopropylethylamine. This mixture was allowed to stir until all reagents were dissolved and then the solution was cooled to 0 °C using an ice bath. In a separate flask, 3.08 g (0.02 mol) of 1,8-diaminonaphthalene was dissolved in 10 mL of dry THF. Using a 20 mL syringe, the solution of 1,8-diaminonaphthalene was then added to the flask containing 2,6-pyridinedicarbonyl dichloride and *N,N*-diisopropylethylamine over 60 s to yield a cloudy off-white mixture, which was stirred at 0 °C for 2 h. An off-white solid was collected by filtration, washed with boiling methanol (3 × 40 mL) and then with 20 mL of diethyl ether. It was then dried under vacuum for 8 h (4.0 g, 71%). ^1H -NMR (400 MHz, DMSO-*d*₆) δ (ppm): 11.25 (s, 4H, NHCO), 7.99 (m, 4H, CHPy), 7.89 (m, 6H, CH), 7.60 (m, 8H, C-H). ^{13}C NMR (400 MHz, DMSO-*d*₆) δ (ppm): 161.4, 148.3, 139.3, 135.6, 132.6, 127.7, 126.5, 125.7, 124.3. HR-MS (ESI, MeOH) *m/z*: $[\text{H}_3\text{L}^2]^-$ Calcd. for $[\text{C}_{34}\text{H}_{21}\text{N}_6\text{O}_4]^-$ 577.162; found 577.129; *m/z*: $[\text{H}_4\text{L}^2 + \text{Cl}]^-$ Calcd. for $[\text{C}_{34}\text{H}_{22}\text{ClN}_6\text{O}_4]^-$ 613.139; found 613.102 (Figures S9 – S11). Anal. Calc. for $\text{C}_{34}\text{H}_{28}\text{N}_6\text{O}_7$: C, 64.55; H, 4.46; N, 13.28. Found: C, 64.50; H, 4.29; N, 12.98. X-Ray quality crystals were obtained as white needles via slow diffusion of Et_2O into a concentrated solution of H_4L^2 in DMF.

H_2L^3 .

To a 500 mL round bottom flask that was pre-flushed with N_2 , 200 mL of dry THF were added. Under an active flow of N_2 , 1,8-diaminonaphthalene (0.500 g, 0.003 mol) was added forming a deep red-brown solution immediately. The 1,8-diaminonaphthalene solution was heated to 40 °C. In a N_2 glovebox, 2,6-pyridinedicarbonyl dichloride (0.645 g, 0.003 mol) was dissolved in 25 mL of dry THF. The 2,6-pyridinedicarbonyl dichloride solution was taken-up in a 50 mL syringe equipped with a 9" steel needle. The 2,6-pyridinedicarbonyl solution was added to the 40 °C 1,8-diaminonaphthalene solution via syringe pump at a rate of ~ 1 drop/sec over 8 h (2.0 $\mu\text{L}/\text{min}$). A red solid precipitated from solution and was left to stir overnight. The mixture was then filtered via vacuum filtration over a 30 mL Buchner

funnel. The solid was washed with 100 mL of pentane (0.851 g, 69%). Further purification of H_2L^3 was obtained via slow diffusion of pentane into a concentrated solution of H_2L^3 in DMF. ^1H -NMR (300 MHz, $\text{DMSO}-d_6$) δ (ppm): 8.60 (d, J = 7.9 Hz, 2H, CHPy), 8.32 (t, J = 7.9 Hz, 1H, CH), 7.27 (dd, J = 8.3, 7.2 Hz, 4H, CH), 7.19 (d, J = 8.2 Hz, 4H, CH), 6.92 (d, J = 7.2 Hz, 4H, CH). HR-MS (ESI, THF) m/z : $[\text{H}_2\text{L}^3]^-$ Calcd. for $[\text{C}_{27}\text{H}_{16}\text{N}_5]^-$ 410.1396; found 410.0821; $[\text{H}_3\text{L}^3]^-$ Calcd. for $[\text{C}_{27}\text{H}_{18}\text{N}_5\text{O}]^-$ 428.1502; 428.0877; $[\text{H}_2\text{L}^3 \text{Cl}]^-$ Calcd. for $[\text{C}_{27}\text{H}_{17}\text{N}_5\text{Cl}]^-$ 446.1184; 446.0597. X-Ray quality crystals were obtained as red-brown blocks via slow diffusion of pentane into a concentrated solution of H_2L^3 in DMF (Figures S12 – S14, Table S1).

$\text{K}(\text{THF})[\text{L}^2\text{Cu}_2(\text{CH}_3\text{CONH})]$.

To a 50 mL Schlenk flask, 200 mg (0.35 mmol) H_4L^2 , 310 mg (0.86 mmol) of $\text{Cu}(\text{OTf})_2$, and 20 mL of dry CH_3CN were added and the resulting mixture allowed to stir for 10 min. To the suspension, 1.0 mL of a 2.18 M solution of NMe_4OH in MeOH was added, resulting in a color change to a deep green. After stirring for 1 h, solvent was removed under vacuum to bring the volume to ~5 mL. Diethyl ether (20 mL) was added, resulting in the precipitation of green powder that was collected by filtration, washed with Et_2O (2×20 mL) and allowed to dry (96 mg, 33%). Crystals were obtained by addition of KOTf to the CH_3CN solution. Repeated attempts to obtain accurate and reproducible CHN analysis for $\text{K}(\text{THF})[\text{L}^2\text{Cu}_2(\text{CH}_3\text{CONH})]$ and the following complexes were unsuccessful, which we attribute to incomplete combustion.

$[\text{NMe}_4]_2[\text{L}^2\text{Cu}_2(\text{CO}_3)]$.

This compound was prepared analogously to $\text{K}(\text{THF})[\text{L}^2\text{Cu}_2(\text{CH}_3\text{CONH})]$ except a 3:1 mixture of pyridine/water was used as the solvent instead of CH_3CN . The resulting mixture was then allowed to crystallize open to air to afford green crystals of $[\text{NMe}_4]_2[\text{L}^2\text{Cu}_2(\text{CO}_3)]$ (165 mg, 52%). $[\text{NMe}_4]_2[\text{L}^2\text{Cu}_2(\text{OMe})(\text{MeOH})_2] \cdot (\text{H}_2\text{O})(\text{OTf})(\text{MeOH})$. This compound was prepared analogously to $\text{K}(\text{THF})[\text{L}^2\text{Cu}_2(\text{CH}_3\text{CONH})]$ except MeOH was used as the solvent medium instead of CH_3CN to afford a green powder (76 mg, 25%). Single crystals were obtained by slow evaporation of Et_2O in concentrated MeOH solutions of the complex.

4. Results and Discussion

4.1.1. Ligand Synthesis

A synthesis of the ligand precursor HL^1 was reported previously involving the treatment of 2-aminomethyl substituted quinoline with $\text{Cu}(\text{OAc})_2$ to yield a $\text{Cu}(\text{II})$ complex $[\text{L}^1\text{Cu}(\text{OAc})(\text{H}_2\text{O})]$, followed by removal of $\text{Cu}(\text{II})$ with Na_2EDTA [8]. We developed a different, more classical synthetic organic route deemed potentially more amenable to larger scale preparations (Scheme 1). This route involved precedent [10] reaction of quinaldic acid with 1(methanesulfonyl)benzotriazole to yield 2-quinolyl(acylbenzotriazole) (**1**, 55%, ~4 g scale), which upon treatment with NH_4OH and deprotonation with KH yielded the potassium salt of the 2quinolinecarboximido anion, **2**, that was isolated as a solid (57%). Subsequent reaction with 2quinaldoyl chloride yielded HL^1 (51%).

In an initial attempt to prepare H_4L^2 we reacted 2,6-pyridinedicarbonyl dichloride with 1,8-diaminonaphthalene in the presence of $NEt_2(iPr)$, using slow addition of the latter to the former with the aim of favoring macrocyclization over oligomerization. Analysis of the products resulting from this reaction revealed a mixture (by ESI-MS) of the desired product H_4L^2 and a bright red compound (in variable amounts) identified by NMR spectroscopy, ESI-MS, and X-ray crystallography as (2,6-diperimidine)pyridine **3** (Scheme 2, Figures S12 – S14). We rationalize the formation of **3** as involving initial addition of an amino group to the acyl chloride to give an intermediate amide with one free amino group that then undergoes a favorable second condensation (with loss of water, catalyzed by HCl that is available in the absence of added base) to yield the 6-membered ring of the perimidine (Scheme 3).

Working under the assumption that the ring-closing condensation was slower than the initial addition of the amine to the acyl chloride, we changed the reaction protocol by inverting the order of addition of the reagents. Importantly, we also found that by cooling a concentrated THF solution of the 2,6-pyridinedicarbonyl dichloride and *N,N*-diisopropylethylamine to $\sim 0^\circ C$ and adding a THF solution of 1,8-diaminonaphthalene rapidly (~ 1 min), H_4L^2 precipitated in 71% yield on a ~ 4 g scale (and formation of **3** was avoided). The product was identified on the basis of 1H NMR spectroscopy, high resolution mass spectrometry, and X-ray crystallography (Figure 2, crystals grown by vapor diffusion of Et_2O into a dimethylacetamide (DMA) solution). In the crystal structure, the pyridyl rings are approximately parallel to each other, with the naphthyl planes splayed to orient the amide N-H groups so that they hydrogen bond with a DMA solvate molecule. Such binding of solvate by H_4L^2 is preceded, as other carboxamide macrocycles are known to be good receptors for anions and polar organic molecules [15]. Importantly, the observed geometry for H_4L^2 differs significantly from that of **C** (Figure 1), which adopts a much flatter shape [7c], portending different structures for their dicopper complexes (see below).

4.2.2. Synthesis and characterization of complexes.

4.2.2.1. Complexes Derived from HL^1 .—With the aim of preparing a mononuclear Cu(I) complex that would model the LPMO active site, we reacted HL^1 with Cu(I)-mesityl (Scheme 4). A dark brown product was isolated and characterized by NMR spectroscopy, CHN analysis, and X-ray crystallography. The 1H NMR spectrum of the product features 6 appropriately split aromatic resonances shifted upfield relative to those of HL^1 , indicating coordination to a metal ion and identical chemical environments for the quinolyl rings (Figure S6). The X-ray crystal structure revealed that instead of adopting the anticipated mononuclear topology, the complex is a symmetric dimer $(L^1Cu)_2$, with each bis(quinolyl)amide ligand binding via two N-donors to one Cu(I) ion and the third binding the other Cu(I) center (Figure 3). The $[Cu_2(\mu-NR_2)_2]$ core geometric features are analogous to those reported previously for a dimer similarly bridged by PN-P ‘pincer’ ligands comprising di(aryl)amide bridges [16], but with the Cu-Cu distance being slightly shorter (2.6132(5) Å vs. 2.7283(3) Å) and the amide N-Cu distances slightly longer (avg. 2.24 Å vs. 2.15 Å) for $(L^1Cu)_2$ (Table 1).

Two Cu(II) complexes were prepared, one by exposure of $(\mathbf{L}^1\text{Cu})_2$ to air at room temperature and the other by treatment of HL^1 with $\text{Cu}(\text{OTf})_2$ in 90% EtOH (Scheme 4). The complexes were identified by analytical data and X-ray crystallography as $\mathbf{L}^1_2\text{Cu}$ and $[\mathbf{L}^1\text{Cu}(\text{OH}_2)_2]\text{OTf}$, respectively (Figure 4). The structure of the former ($\mathbf{L}^1_2\text{Cu}$) exhibited whole molecule disorder, which was modeled such that the structure was inverted on a mirror plane dissecting the copper center and the N_{amide} atoms (there was no evidence of twinning or solvent disorder). The bond lengths reported for the major structure (~92%) were deemed reliable, so only these parameters are reported in this discussion. The structure of $\mathbf{L}^1_2\text{Cu}$ shows a Jahn-Teller ‘compressed’ octahedral geometry, with the two similar Cu- N_{amide} distances (Cu1-N1 or -N3 1.943(17) and 1.935(17) Å) significantly shorter than the four (two by symmetry) Cu- $\text{N}_{\text{quinolyl}}$ distances (2.284(15) and 2.299(15) Å) (Table 1). Attempts to monitor the formation of $\mathbf{L}^1_2\text{Cu}$ upon reaction of $(\mathbf{L}^1\text{Cu})_2$ with O_2 at temperatures ranging from $-40\text{ }^\circ\text{C}$ to $25\text{ }^\circ\text{C}$ in a variety of solvents (e.g. CH_2Cl_2 , dimethyl sulfoxide) while monitoring via UV-vis spectroscopy showed immediate decay of the features at 465 nm and 510 nm, but no new features that could be ascribed to a copperoxygen species. The structure of the cationic portion of $[\mathbf{L}^1\text{Cu}(\text{OH}_2)_2](\text{OTf})$ is analogous to that of the previously reported complex $\mathbf{L}^1\text{Cu}(\text{OH}_2)(\text{OAc})$ [8], insofar as it features the $\mathbf{L}^1$ anion coordinated to a single Cu(II) ion in *mer* fashion with two other monodentate O donors. The tau values of $[\mathbf{L}^1\text{Cu}(\text{OH}_2)_2]\text{OTf}$ ($\tau_5 = 0.60$) and $\mathbf{L}^1\text{Cu}(\text{OH}_2)(\text{OAc})$ ($\tau_5 = 0.05$) differ significantly, such that $[\mathbf{L}^1\text{Cu}(\text{OH}_2)_2]\text{OTf}$ exhibits a distorted trigonal bipyramidal geometry and $\mathbf{L}^1\text{Cu}(\text{OH}_2)(\text{OAc})$ is a nearly ideal square pyramid. An additional difference is the presence of hydrogen-bonding in $[\mathbf{L}^1\text{Cu}(\text{OH}_2)_2]\text{OTf}$ involving one of the bound water molecules and the O atom in the triflate counteranion.

4.2.2.1. Complexes Derived from H_4L^2 .—With the aim of preparing μ -hydroxo-bridged dicopper complexes for comparison to such species characterized previously supported by ligand **C** (Figure 1, [7c]), we treated H_4L^2 with $\text{Cu}(\text{OTf})_2$ and excess Me_4NOH (in CH_3CN , pyridine/ H_2O , or MeOH). Crystals of complexes with anions of general formula $[\mathbf{L}^2\text{Cu}_2(\text{X})]^{n-}$ were isolated, where $\text{X} = \text{CH}_3\text{CONH}$ ($n = 1$), CO_3^{2-} ($n = 2$), or MeO^- ($n = 1$) (Scheme 5). Unfortunately, all attempts to assess purity of the bulk material obtained in each case were unsuccessful, but we were able to obtain structural information by X-ray crystallography nonetheless (Figure 5, Table 2).

The X-ray structures reveal the $(\mathbf{L}^2)^{4-}$ ligand binding to two Cu(II) ions in a conformation yielding an open paddle-wheel geometry, with an additional bridging ligand completing the square planar coordination sphere of each metal ion. The open paddlewheel motif differs from the more ‘open’ puckered geometry for **C** [7], clearly indicating the effect of the differing aromatic spacers between the pyridine(dicarboxamide) units. The three structures differ with respect to that additional bridging ligand, which appears to derive from the solvent (MeOH) or hydrolysis of the solvent (CH_3CN , to yield CH_3CONH^-) or CO_2 in air (to yield CO_3^{2-}). Such hydrolysis may be promoted by an intermediate copper-hydroxide species, but no such species was observed. The methoxide-bridged structure was co-crystallized with an equivalent of tetramethylammonium triflate with a problematic triflate anion lying on a mirror plan and possessing both symmetrical and rotational disorder. This particular crystallographic model required omission of H-atoms on the

tetramethylammonium cations as well as the methanol/methoxides for the refinement to properly converge to the most appropriate model.

5. Conclusions

After developing useful synthetic routes to known ligand HL^1 and new ligand H_2L^2 , a variant of **C** (Figure 1) with a naphthyl rather than a phenyl spacer, their copper coordination chemistry was explored. The reaction of HL^1 with copper(I) mesityl yielded a dinuclear complex in which each bis(quinolyl)amide ligand binds via two N-donors to one Cu(I) ion and via the third to the other Cu(I) center. While examples of related dimers generate Cu/O₂ adducts upon oxygenation [17], such chemistry was not seen with $(\text{L}^1\text{Cu})_2$; instead, only formation of an octahedral Cu(II) complex L^1_2Cu was observed upon exposure of $(\text{L}^1\text{Cu})_2$ to air. We speculate that installation of sterically encumbered substituents into HL^1 may circumvent these pathways and enable isolation of novel Cu/O₂ species.

Reactions of H_4L^2 with $\text{Cu}(\text{OTf})_2$ and excess Me_4NOH in various solvents yielded complexes with anions of general formula $[\text{L}^2\text{Cu}_2(\mu\text{-X})]^n$, where $\text{X} = \text{CH}_3\text{CONH}$ ($n = 1$), CO_3^{2-} ($n = 2$), or MeO^- ($n = 1$). These complexes displayed open paddle-wheel geometries that differed from the more ‘open’ puckered structures reported previously using ligand **C** [7], clearly indicating a distinct influence of the naphthyl spacer in the ligand. This observation from X-ray crystallography may have implications for reactivity studies that are the subject of future work.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

We thank the National Institutes of Health (grant R37GM47365) for funding the research reported herein, and Dr. Victor G. Young, Jr., for assistance with the X-ray crystallography. We are also grateful for the procurement of the Bruker-AXS D8 Venture Diffractometer via a grant awarded by NSF/MRI (No. 1229400) and the University of Minnesota.

References

- [1]. Solomon EI, Heppner DE, Johnston EM, Ginsbach JW, Cirera J, Qayyum M, Kieber-Emmons MT, Kjaergaard CH, Hadt RG, Tian L, Chem. Rev 114 (2014), 3659–3853. 10.1021/cr400327t [PubMed: 24588098]
- [2]. (a) Mirica LM, Ottenwaelde X, Stack TDP, Chem. Rev 104 (2004), 1013–1045. 10.1021/cr020632z [PubMed: 14871148] (b) Lewis EA, Tolman WB, Chem. Rev 104 (2004), 1047–1076. 10.1021/cr020633r [PubMed: 14871149] (c) Elwell CE, Gagnon NL, Neisen BD, Dhar D, Spaeth AD, Yee GM, Tolman WB, Chem. Rev 117 (2017), 2059–2107. 10.1021/acs.chemrev.6b00636 [PubMed: 28103018] (d) Quist DA, Diaz DE, Liu JJ, Karlin KD, J. Biol. Inorg. Chem 22 (2017), 253–288. 10.1007/s00775-016-14152 [PubMed: 27921179] (e) Itoh S, Abe T, Morimoto Y, Sugimoto H, Inorg. Chim. Acta, 481 (2018), 38–46. 10.1016/j.ica.2017.09.017.
- [3]. For example, see: de Oliveira FT, Chanda A, Banerjee D, Shan X, Mondal S, Que L Jr, Bominaar EL, Münck E, Collins TJ, Science, 315 (2007), 835–838. 10.1126/science.1133417 [PubMed: 17185561]
- [4]. Selected examples: (a) Diaddario LL, Robinson WR, Margerum DW, Inorg. Chem 22 (1983), 1021–1025. 10.1021/ic00149a004 (b) Anson FC, Collins TJ, Richmond TG, Santarsiero BD, Toth

JE, Treco BGRT, J. Am. Chem. Soc 109 (1987), 2974–2979, 10.1021/ja00244a020 and references cited therein.

- [5]. Kumar P, Gupta R, Dalton Trans. 45 (2016), 18769–18783. 10.1039/C6DT03578G [PubMed: 27819372]
- [6]. (a)Donoghue PJ, Tehranchi J, Cramer CJ, Sarangi R, Solomon EI, Tolman WB, J. Am. Chem. Soc 133 (2011), 17602–17605. 10.1021/ja207882h. [PubMed: 22004091] (b)Tehranchi J, Donoghue PJ, Cramer CJ, Tolman WB, Eur. J. Inorg. Chem (2013) 2013, 4077–4084. 10.1002/ejic.201300328.(c)Dhar D, Tolman WB, J. Am. Chem. Soc 137 (2015), 1322–1329. 10.1021/ja512014z. [PubMed: 25581555] (d)Gagnon N, Tolman WB, Acc. Chem. Res 48 (2015), 2126–2131. 10.1021/acs.accounts.5b00169. [PubMed: 26075312] (e)Dhar D, Yee GM, Spaeth AD, Boyce DW, Zhang H, Dereli B, Cramer CJ, Tolman WB, J. Am. Chem. Soc 138 (2016), 356–368. 10.1021/jacs.5b10985. [PubMed: 26693733] (f)Dhar D, Yee GM, Markle TF, Mayer JM, Tolman WB, Chem. Sci 8 (2017), 1075–1085. 10.1039/C6SC03039D. [PubMed: 28572905] (g)Spaeth AD, Gagnon NL, Dhar D, Yee GM, Tolman WB, J. Am. Chem. Soc 139 (2017), 4477–4485. 10.1021/jacs.7b00210. [PubMed: 28319386] (h)Dhar D, Yee GM, Tolman WB, Inorg. Chem 57 (2018), 9794–9806. 10.1021/acs.inorgchem.8b01529. [PubMed: 30070473]
- [7]. (a)Halvagar MR, Neisen B, Tolman WB, Inorg. Chem 52 (2012), 793–799. 10.1021/ic301914u. [PubMed: 23268657] (b)Halvagar MR, Tolman WB, Inorg. Chem 52 (2013), 8306–8308. 10.1021/ic401446s. [PubMed: 23886308] (c)Halvagar MR, Solntsev PV, Lim H, Hedman B, Hodgson KO, Solomon EI, Cramer CJ, Tolman WB, J. Am. Chem. Soc 136 (2014), 7269–7272. 10.1021/ja503629r. [PubMed: 24821432]
- [8]. Sahu R, Padhi SK, Jena HS, Manivannan V, Inorg. Chim. Acta 363 (2010), 1448–1454. 10.1016/j.ica.2010.01.028
- [9]. Ciano L, Davies GJ, Tolman WB, Walton PH, Nature Catalysis 1 (2018), 1, 571–577. 10.1038/s41929-018-0110-9
- [10]. Katritzky AR, He H-Y, Suzuki K, J. Org. Chem 65 (2000), 8210–8213. 10.1021/jo000792f [PubMed: 11101375]
- [11]. Tsuda T, Yazawa T, Watanabe K, Fujii T, Saegusa T, J. Org. Chem 46 (1981), 192–194. 10.1021/jo00314a048
- [12]. Sheldrick GM, Acta Cryst. A 64 (2008), 112–122. DOI: 10.1107/S0108767307043930 [PubMed: 18156677]
- [13]. Pramanik MMD, Rastogi N, Org. Biomol. Chem 14 (2016), 1239–1243. 10.1039/C5OB01975C [PubMed: 27186609]
- [14]. (a)Zhang Z, Zheng D, Wan Y, Zhang G, Bi J, Liu Q, Liu T, Shi L, J. Org. Chem 83 (2018), 1369–1376. 10.1021/acs.joc.7b02880. [PubMed: 29302966] (b)Mete TB, Singh A, Bhat RG, Tet. Lett 58 (2017), 4709–4712. 10.1016/j.tetlet.2017.11.006.(c)Hansen EC, Pedro DJ, Wotal AC, Gower NJ, Nelson JD, Caron S, Wiex DJ, Nat. Chem 8 (2016), 1126–1130. 10.1038/nchem.2587. [PubMed: 27874864] (d)Tomas-Mendivil E, Francos J, Gonzalez-Fernandez R, Gonzalez-Liste PJ, Borge J, Cadierno V, Dalton Trans, 45 (2016), 13590–13603. 10.1039/C6DT02375D. [PubMed: 27510460] (e)Ma B, Xie H, Li J, Zhan H, Lin K, Liu W, J. Molec. Cat. A: Chemical, 420 (2016), 290–293. 10.1016/j.molcata.2016.04.031.(f)Huang Y, Chen T, Li Q, Zhou Y, Yin S, Org. Biomol. Chem 13 (2015), 7289–7293. 10.1039/C5OB00685F. [PubMed: 26054841] (g)Xie A, Cao M, Liu Y, Feng L, Hu X, Dong W, Eur. J. Org. Chem 2014 (2014), 436–441. 10.1002/ejoc.201301364.(h)Battilocchio C, Hawkins JM, Ley SV, Org. Lett 16 (2014), 1060–1063. 10.1021/ol403591c. [PubMed: 24495110] (i)Wang Y, Yamaguchi K, Mizuno N, Angew. Chem. Int. Ed 51 (2012), 7250–7253. 10.1002/anie.201203098.(j)Caronna T, Gambarotti C, Palmisano L, Punta C, Recupero F, Chem. Commun (2003), 2350–2351. 10.1039/B306140J.(k)Khalafi-Nezhad A, Mokhtari B, Rad MNS, Tet. Lett 44 (2003), 7325–7328. 10.1016/S0040-4039(03)01866-5.(l)Minisci F, Recupero F, Punta C, Gambarotti C, Antonietti F, Fontana F, Pedulli GF, Chem. Commun (2002), 2496–2497. 10.1039/B206192A.(m)Jones RCF, Smallridge MJ, Chapleo CB, J. Chem. Soc., Perkin Trans 1, (1990), 385–391. 10.1039/P19900000385.
- [15]. (a)Anion Coordination Chemistry; Bowman-James K; Bianchi A; García-España E, Eds.; Wiley-VCH: Weinheim, 2012.(b)Bowman-James K, Acc. Chem. Res 38 (2005), 671–678. 10.1021/

ar040071t [PubMed: 16104690] (c)Kang SO, Powell D, Day VW, Bowman-James K, Crystal Growth & Design 7 (2007), 606–608. 10.1021/cg0608817

- [16]. Harkins SB, Mankad NP, Miller AJM, Szilagyi RK, Peters JC, J. Am. Chem. Soc 130 (2008), 3478–3485. 10.1021/ja076537v [PubMed: 18298114]
- [17]. (a)Carrier SM, Ruggiero CE, Houser RP, Tolman WB, Inorg. Chem 32 (1993), 4889–4899. 10.1021/ic00074a039(b)Kitajima N, Fujisawa K, Moro-oka Y, Toriumi K, J. Am. Chem. Soc 111 (1989), 8975–8976. 10.1021/ja00206a06.

Highlights.

- Mono- and dinuclear copper complexes supported by HL¹ and H₄L² were prepared and characterized, including by X-ray crystallography.
- Mono- and dicopper complexes supported by anionic L¹⁻ revealed its ability to bind both copper(I) and (II) and the lack of steric encumbrance gave rise to dimerization
- Dicopper complexes supported by tetraanionic (L²⁻)⁴⁻ revealed open paddle-wheel geometries with variable bridging ligands (CH₃CONH⁻, CO₃²⁻, MeO⁻)

Previous work: **This work:**

Figure 1. Carboxamide ligand precursors. R = iPr or Me, X = H, NO₂, NMe₃⁺, or SO₃⁻.

Figure 2.

(top) Representation of the X-ray crystal structure of $\text{H}_4\text{L}^2\cdot\text{DMA}$, with dashed lines indicating hydrogen bonds and selected atoms labeled. All hydrogen atoms except those involved in the hydrogen bonds are shown, with all nonhydrogen atoms depicted as 50% thermal ellipsoids. (bottom) Alternate view, rotated $\sim 90^\circ$ to illustrate approximately parallel pyridyl rings (DMA molecule not shown).

Figure 3.

Representation of the X-ray crystal structure of $(\mathbf{L}^1\text{Cu})_2$, showing one of two molecules in the asymmetric unit, all nonhydrogen atoms as 50% thermal ellipsoids, and heteroatoms labeled. Selected bond distances (Å) and angles (deg): Cu1 – Cu1', 2.6132(5); Cu1 – N1, 1.9528(12); Cu1 – N2, 2.2350(14); Cu1 – N3, 1.9501(12); N2 – Cu1 – N2', 108.26(4); N1 – Cu1 – N3, 163.69(6); N1 – Cu1 – N2, 80.62(5).

Figure 4.

Representations of the X-ray crystal structures of (top) L_2Cu and (bottom) $[\text{L}^1\text{Cu}(\text{OH}_2)_2]\text{OTf}$, showing all nonhydrogen atoms as 50% thermal ellipsoids and heteroatoms labeled. Selected bond distances ($\text{\AA}$) and angles (deg) for L_2Cu : Cu1 – N1, 1.943(17); Cu1 – N2, 2.284(15); Cu1 – N3, 1.935(17); Cu1 – N4, 2.284(15); N1 – Cu1 – N3, 180.0; N4 – Cu1 – N4', 155.4(13), N2 – Cu1 – N2', 159.4(11). Selected bond distances ($\text{\AA}$) and angles (deg) for $[\text{L}^1\text{Cu}(\text{OH}_2)_2]\text{OTf}$: Cu1 – N1, 2.0118(19); Cu1 – N2, 1.9264(19);

Cu1 – N3, 2.017(2); Cu1 – O20, 2.017(18); Cu1 – O21, 2.1408(18); H1 – O3, 1.94(5); N1 – Cu1 – N3, 164.59(8); N2 – Cu1 – O20, 128.49(8).

Author Manuscript

Author Manuscript

Author Manuscript

Author Manuscript

Figure 5.

Representations of the X-ray crystal structures of (a) $\text{K(THF)[L}^2\text{Cu}_2(\mu\text{-CH}_3\text{CONH})]$, (b) the anionic portion of $[\text{NMe}_4][\text{L}^2\text{Cu}_2(\mu\text{-CO}_3)] \cdot 4\text{H}_2\text{O}$, and (c) the anionic copper-containing portion of $[\text{NMe}_4]_2[\text{L}^2\text{Cu}_2(\text{OMe})(\text{MeOH})_2] \cdot (\text{H}_2\text{O})(\text{OTf})(\text{MeOH})$. All nonhydrogen atoms are shown as 50% ellipsoids, in addition to H atoms on the CH_3CONH^- and MeOH ligands and those for the water molecules involved in hydrogen bonding to the CO_3^{2-} ligand.

Selected bond distances (Å) and angles (deg) for $\text{K(THF)[L}^2\text{Cu}_2(\mu\text{-CH}_3\text{CONH})]$: Cu1 – Cu2, 2.780(1); Cu1 – N7, 1.914(5); Cu2 – O1, 1.922(5); N2 – Cu1 – N7, 175.53(21); N1 – Cu1 – N3, 160.43(20); N5 – Cu2 – O1, 178.75(21); N4 – Cu2 – N6, 160.41(20). $[\text{NMe}_4][\text{L}^2\text{Cu}_2(\mu\text{-CO}_3)] \cdot 4\text{H}_2\text{O}$: Cu1 – Cu1', 2.7172(7); Cu1 – O3, 1.900(2); Cu2 – O3', 1.900(2); N2 – Cu1 – O3, 175.47(7); N1 – Cu1 – N3, 161.23(8). $[\text{NMe}_4]_2[\text{L}^2\text{Cu}_2(\text{OMe})(\text{MeOH})_2] \cdot (\text{H}_2\text{O})(\text{OTf})(\text{MeOH})$: Cu1 – Cu1', 2.7288(15); Cu1 – N1, 2.023(6); Cu1 – N2, 1.936(5); Cu1 – N3, 2.029(5); Cu1 – O3, 1.949(4); Cu1 – O4, 2.229(5); N1 – Cu1 – N3, 159.4(2); N2 – Cu1 – O3, 147.98(19); N2 – Cu1 – O4, 110.4(2).

Scheme 1.
Synthesis of HL¹.

Scheme 2.

Synthesis of H_4L^2 and **3**. Relative amounts of the two products depended on addition order of reagents, as described in the text..

Scheme 3.

Proposed mechanism for the perimidene ring formation in **3**..

Scheme 4.
Synthesis of complexes derived from HL¹.

Scheme 5.
Synthesis of complexes from H_4L^2 .

Table 1.Crystallographic structure details for $(\mathbf{L}^1\mathbf{Cu})_2$, $\mathbf{L}^1_2\mathbf{Cu}$ and $[\mathbf{L}^1\mathbf{Cu}(\mathbf{OH}_2)_2](\text{OTf})$.

	$(\mathbf{L}^1\mathbf{Cu})_2$	$\mathbf{L}^1_2\mathbf{Cu}$	$[\mathbf{L}^1\mathbf{Cu}(\mathbf{OH}_2)_2](\text{OTf})$
Formula	$\text{C}_{40}\text{H}_{24}\text{Cu}_2\text{N}_6\text{O}_4$	$\text{C}_{40}\text{H}_{24}\text{CuN}_6\text{O}_4$	$\text{C}_{20}\text{H}_{16}\text{CuN}_3\text{O}_4, \text{CF}_3\text{O}_3\text{S}$
Formula Weight (g mol^{-1})	779.73	716.19	574.97
Crystal dimensions (mm)	$0.18 \times 0.22 \times 0.20$	$0.19 \times 0.22 \times 0.19$	$0.21 \times 0.28 \times 0.13$
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	C2/c (No. 15)	C2/c (No. 15)	P2 ₁ /c (No. 14)
<i>Unit cell parameters</i> ^a <i>a</i> (Å)	14.5131(8)	13.8767(11)	14.0530(4)
<i>b</i> (Å)	17.6490(8)	15.7761(12)	18.2106(5)
<i>c</i> (Å)	16.2346(8)	13.8535(11)	8.8417(2)
β (°)	103.288(2)	90.708(3)	107.663(1)
<i>V</i> (Å ³)	4047.0(4)	3032.6(4)	2156.04(10)
<i>Z</i>	4	4	4

^aObtained from least-squares refinement of 4124 reflections with $4.01^\circ < 2\theta < 74.65^\circ$ for $(\mathbf{L}^1\mathbf{Cu})_2$, 4630 reflections with $2.44^\circ < 2\theta < 30.56^\circ$ for $\mathbf{L}^1_2\mathbf{Cu}$ and 8233 reflections with $2.24^\circ < 2\theta < 33.18^\circ$ for $[\mathbf{L}^1\mathbf{Cu}(\mathbf{OH}_2)_2](\text{OTf})$.

Table 2.

Crystallographic structure details for $\text{K}(\text{THF})[\text{L}^2\text{Cu}_2(\mu\text{-CH}_3\text{CONH})]$, $[\text{NMe}_4][\text{L}^2\text{Cu}_2(\mu\text{-CO}_3)]\cdot 4\text{H}_2\text{O}$ and $[\text{NMe}_4]_2[\text{L}^2\text{Cu}_2(\text{OMe})(\text{MeOH})_2]\cdot (\text{H}_2\text{O})(\text{OTf})(\text{MeOH})$.

	$\text{K}(\text{THF})[\text{L}^2\text{Cu}_2(\mu\text{-CH}_3\text{CONH})]$	$[\text{NMe}_4][\text{L}^2\text{Cu}_2(\mu\text{-CO}_3)]\cdot 4\text{H}_2\text{O}$	$[\text{NMe}_4]_2[\text{L}^2\text{Cu}_2(\text{OMe})(\text{MeOH})_2]\cdot (\text{H}_2\text{O})(\text{OTf})(\text{MeOH})$
Formula	$\text{C}_{36}\text{H}_{22}\text{Cu}_2\text{N}_7\text{O}_5, \text{K}, \text{C}_4\text{O}$	$\text{C}_{17.5}\text{H}_9\text{CuN}_3\text{O}_{3.5}, 4 \text{H}_2\text{O}, \text{C}_4\text{H}_{12}\text{N}$	$\text{C}_{18.5}\text{H}_{10}\text{CuN}_3\text{O}_{3.5}, \text{C}_2\text{N}_{0.5}, \text{C}_2\text{N}_{0.5}, \text{C}_{0.5}\text{F}_{1.5}\text{S}_{0.5}\text{O}_{1.5}, \text{CO}, \text{O}_{0.5}$
Formula Weight (g mol^{-1})	862.82	527.03	566.43
Crystal dimensions (mm)	$0.18 \times 0.21 \times 0.19$	$0.24 \times 0.18 \times 0.19$	$0.17 \times 0.22 \times 0.25$
Crystal System	Monoclinic	Monoclinic	Orthorhombic
Space Group	$\text{P2}_1/\text{c}$ (No. 14)	$\text{C2}/\text{c}$ (No. 15)	Ama2 (No. 40)
Unit cell parameters ^a a (Å)	15.2152(16)	19.960(2)	14.2199(6)
b (Å)	17.3574(19)	15.2091(18)	18.2600(8)
c (Å)	15.9778(17)	15.7094(19)	20.8651(8)
β (°)	109.716(2)	104.396(2)	90
V (Å ³)	3972.3(7)	4619.3(10)	5417.7(7)
Z	4	8	8

^aObtained from least-squares refinement of 8067 reflections with $4.21^\circ < 2\theta < 26.34^\circ$ for $\text{K}(\text{THF})[\text{L}^2\text{Cu}_2(\mu\text{-CH}_3\text{CONH})]$, 4691 reflections with $3.70^\circ < 2\theta < 74.79^\circ$ for $[\text{NMe}_4][\text{L}^2\text{Cu}_2(\mu\text{-CO}_3)]\cdot 4\text{H}_2\text{O}$ and 5381 reflections with $3.22^\circ < 2\theta < 74.56^\circ$ for $[\text{NMe}_4]_2[\text{L}^2\text{Cu}_2(\text{OMe})(\text{MeOH})_2]\cdot (\text{H}_2\text{O})(\text{OTf})(\text{MeOH})$.