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

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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 the results of previous work on 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^{2–}) 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

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] as well as $[CuOCu]^{n+}$ (n = 2-4) species in methane monooxygenase^[5] and heterogeneous Cu-doped zeolites,^[6] we and others have aimed to synthesize and study in detail reactive mono- and dicopper complexes containing these and related cores.^[1,7] In recent work,^[8,9] we prepared compounds 1 and 2 proposed to contain [Cu^{III}OH]²⁺ and [Cu^{II/III}(OH)Cu^{III}]^{4+/5+} moieties using the ligands L1²⁻, L2²⁻, and L3⁴⁻, respectively (Figure 1). The powerful electron-donating ability of the carboxamide donors in the ligands was critical for stabilizing the reactive oxidized cores of these complexes.

oxidations of **3** and **5** at potentials about 300 mV higher than those of 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.

Concerned about the potential redox noninnocence of the ortho-phenylenediamine linkers in L3⁴⁻, and with the aim of further enhancing the electron-donating properties of the carboxamide 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. However, efforts to isolate dicopper complexes of L44- have failed; 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 (H_2L4^{2-}) to the fourth ligand coordinated to the Cu^{II} ion. Such interactions model secondary sphere hydrogen bonding in important metalloenzyme active sites.^[11] It is understood that hydrogen-bond-donating and -accepting residues in the second coordination sphere of active sites of enzymes 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, as there are reports of 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

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Figure 1. Ligands and complexes discussed herein.

up to +126 mV.^[11a] A number of studies aimed at understanding how such hydrogen bonding influences the reactivity and redox properties of metal complexes 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 the redox potentials and/ or the catalytic activity of Cu^{II} complexes.^[13] Herein, we evaluate the structures of a series of monocopper complexes of H₂L4²⁻ and the new purposefully mononucleating ligands H_2L5^{2-} (R' = H or tBu) 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 H₂L4²⁻

Ligand precursor H_4L4 was prepared by using a modified version of the published method.^[10] Initial attempts to generate dicopper complexes of $L4^{4-}$ by treating H_4L4 with an excess amount of base in the presence of Cu^{II} salts (greater than or equal to 2 equiv.) only yielded monocopper complexes 3–5. A more purposeful synthesis was developed by using 2 equiv. of base and 1 equiv. of CuX_2 (Scheme 1). The complexes were isolated as crystalline solids, in modest yields, and characterized by electrospray ionization mass



Scheme 1. Synthesis of complexes of H_2L4^{2-} . (i) NMe₄OH (2 equiv.), CuX₂ (X = Cl, OAc, or OTf). (ii) air, DMF.



Figure 2. Representations of the anionic portions of the X-ray structures of (a) $[NMe_4][H_2L4Cu(Cl)]$ (3), (b) $[NMe_4]-[H_2L4Cu(OAc)]$ (4), and (c) $[NMe_4][H_2L4Cu(OH)]$ (5), showing all non-hydrogen atoms as 50% thermal ellipsoids and hypothesized hydrogen bonds as dashed lines.



Table 1. Selected interatomic distances [Å] and angles [°] for the indicated X-ray crystal structures.

$[NMe_4][(H_2L4)Cu(Cl)]$ (3)							
Cu1–N1	1.986(2)		N4···Cl1	3.393(3)	N2-Cu1-Cl1	178.75(7)	
Cu1-N2	1.926(2)		N6Cl1	3.390(2)	N2-Cu1-N1	80.40(9)	
Cu1–N3	1.984(2)		H4···Cl1	2.602	Cl1-Cu1-N1	99.99(7)	
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)	
[NMe4]][(H	[NMe ₄][(H ₂ L4)Cu(OAc)] (4)						
Cu1–N1	1.980(2)	N4…O1	3.003(2)		N2-Cu1-O1	171.46(6)	
Cu1-N2	1.920(2)	N601	3.002(2)		N2-Cu1-N1	80.97(7)	
Cu1–N3	1.991(2)	H4•••O1	2.202		Ol-Cul-Nl	99.43(6)	
Cul-Ol	1.937(1)	H6•••O1	2.197		N2-Cu1-N3	80.73(7)	
Cul-O2	2.636(2)				O1-Cu1-N3	98.11(6)	
					N1-Cu1-N3	161.31(7)	
[NMe4]][(H	2 L4)Cu(O	H)] (5)					
Cu1–N1	2.005(2)	N4O1	2.890(2)		N2-Cu1-O1	172.85(7)	
Cu1–N2	1.931(2)	N6O1	2.865(2)		N2-Cu1-N1	80.08(7)	
Cu1–N3	2.002(2)	H4•••O1	2.038		Ol-Cul-Nl	99.69(6)	
Cul-Ol	1.884(1)	H6•••O1	2.055		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)					
Cul-N1	1.982(2)	N4•••O1	2.957(4)		N2-Cu1-O1	169.46(8)	
Cu1–N2	1.931(2)	N6O1	3.024(4)		N2-Cu1-N1	80.38(9)	
Cu1–N3	1.982(2)	H4•••O1	2.106		Ol-Cul-Nl	99.96(8)	
Cul-Ol	1.960(2)	H6•••O1	2.170		N2-Cu1-N3	80.32(9)	
Cul-O3	2.543(3)	N10O2	3.1939(48)		O1–Cu1–N3	98.30(8)	
Cu2–N7	1.991(2)	N12O2	3.1276(50)		NI-Cul-N3	160.32(9)	
Cu2–N8	1.919(2)	H10O2	2.019		N8-Cu2-O2	177.96(9)	
Cu2–N9	2.019(3)	H12•••O2	1.908		N8-Cu2-N7	80.84(10)	
Cu2-02	1.908(2)				02-Cu2-N/	99.76(10)	
					N8-Cu2-N9	80.50(10)	
					N7 Cu2 N9	98.08(10) 160.35(10)	
[NMedb[{(H- I4)Cu3				117-Cu2-119	100.33(10)	
L=		3(==3)](-)					
0 1 3 11	1 0 7 0 (2)		314 01	0.045(4)			
Cul-N1	1.979(3)		N401	3.045(4)	N2-Cul-Ol	171.37(12)	
Cul–N1 Cul–N2	1.979(3) 1.923(3)		N4•••O1 N6•••O1	3.045(4) 3.167(4)	N2-Cu1-Ol N2-Cu1-N1	171.37(12) 80.68(14)	
Cul–N1 Cul–N2 Cul–N3	1.979(3) 1.923(3) 1.991(3) 1.045(3)		N4•••O1 N6•••O1 H4•••O1	3.045(4) 3.167(4) 2.219 2.305	N2-Cul-Ol N2-Cul-N1 Ol-Cul-N1	171.37(12) 80.68(14) 100.31(12) 80.25(14)	
Cul–N1 Cul–N2 Cul–N3 Cul–O1 Cu2_N7	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.079(3)		N4•••O1 N6•••O1 H4•••O1 H6•••O1	3.045(4) 3.167(4) 2.219 2.395 3.108(4)	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N1 N2-Cu1-N3 O1 Cu1 N2	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu1–O1 Cu2–N7 Cu2–N8	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.919(3)		N4O1 N6O1 H4O1 H6O1 N10O2 N12O2	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4)	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N1 N2-Cu1-N3 O1-Cu1-N3	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu1–O1 Cu2–N7 Cu2–N8 Cu2–N9	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.919(3) 1.975(3)		N4O1 N6O1 H4O1 H6O1 N10O2 N12O2 H10O2	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440	N2-Cu1-OI N2-Cu1-N1 O1-Cu1-N1 N2-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu1–O1 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.919(3) 1.975(3) 1.949(3)		N4O1 N6O1 H4O1 H6O1 N10O2 N12O2 H10O2 H12O2	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N1 N2-Cu1-N3 O1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu1–O1 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.919(3) 1.975(3) 1.949(3) 1.987(4)		N4O1 N6O1 H4O1 H6O1 N10O2 N12O2 H10O2 H12O2 N16O3	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421 3.090(5)	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N1 N2-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu1–O1 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.919(3) 1.975(3) 1.949(3) 1.987(4) 1.931(3)		N401 N601 H401 H601 N1002 N1202 H1002 H1202 N1603 N1803	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421 3.090(5) 2.984(4)	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N1 N2-Cu1-N3 O1-Cu1-N3 N8-Cu2-N3 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu1–O1 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.919(3) 1.975(3) 1.949(3) 1.987(4) 1.931(3) 1.977(4)		N401 N601 H401 H601 N1002 N1202 H1202 H1202 N1603 N1803 H1603	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421 3.090(5) 2.984(4) 2.503	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N1 N2-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu1–O1 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.919(3) 1.975(3) 1.949(3) 1.987(4) 1.931(3) 1.977(4) 1.942(3)		N4O1 N6O1 H4O1 H6O1 N10O2 N12O2 H12O2 H12O2 N16O3 N18O3 H16O3 H18O3	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421 3.090(5) 2.984(4) 2.503 2.398	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N1 N2-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu2–N1 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.919(3) 1.949(3) 1.949(3) 1.987(4) 1.931(3) 1.977(4) 1.942(3)		N401 N601 H401 H601 N1002 H1002 H1002 H1002 H1202 N1603 N1803 H1603 H1803	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.421 3.090(5) 2.984(4) 2.503 2.398	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N1 N2-Cu1-N3 O1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-O3	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.919(3) 1.919(3) 1.949(3) 1.949(3) 1.987(4) 1.937(4) 1.942(3)		N4O1 N6O1 H4O1 H6O1 N10O2 H10O2 H10O2 H12O2 N16O3 N18O3 H16O3 H16O3	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.440 2.441 3.090(5) 2.984(4) 2.503 2.398	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N1 N2-Cu1-N3 O1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-O13 N14-Cu3-N13	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.08(16)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu2–N7 Cu2–N7 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.975(3) 1.975(3) 1.949(3) 1.987(4) 1.931(3) 1.942(3)		N4O1 N6O1 H4O1 H6O1 N10O2 H10O2 H10O2 H10O2 H12O2 N16O3 N18O3 H16O3 H18O3	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421 3.090(5) 2.984(4) 2.503 2.398	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-O3 N14-Cu3-N13 O3-Cu3-N13	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.08(16) 98.16(13)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu2–N7 Cu2–N7 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.945(3) 1.945(3) 1.979(3) 1.975(3) 1.949(3) 1.987(4) 1.931(3) 1.942(3)		N401 N601 H401 H601 N1002 H1002 H1002 H1002 H1003 H1603 H1603 H1803	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.440 2.421 3.090(5) 2.984(4) 2.503 2.398	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-O3 N14-Cu3-N13 O3-Cu3-N13 N14-Cu3-N15	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.16(13) 81.17(16)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu1–O1 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.919(3) 1.987(4) 1.931(3) 1.977(4) 1.942(3)		N4O1 N6O1 H4O1 H6O1 N10O2 N12O2 H10O2 H10O2 H10O3 N18O3 H16O3 H18O3	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.420 2.421 3.090(5) 2.984(4) 2.503 2.398	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N3 N2-Cu1-N3 N1-Cu1-N3 N8-Cu2-N7 N8-Cu2-N7 N8-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-N13 O3-Cu3-N15 O3-Cu3-N15	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.08(16) 98.16(13) 81.17(16) 99.94(13)	
Cul–N1 Cul–N2 Cul–N3 Cul–O1 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.979(3) 1.987(4) 1.931(3) 1.977(4) 1.942(3)		N4O1 N6O1 H4O1 H6O1 N10O2 H10O2 H12O2 H12O2 H12O2 H16O3 H16O3 H18O3	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421 3.090(5) 2.984(4) 2.503 2.398	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-N13 O3-Cu3-N13 N14-Cu3-N15 N13-Cu3-N15	$\begin{array}{c} 171.37(12)\\ 80.68(14)\\ 100.31(12)\\ 80.35(14)\\ 97.95(12)\\ 160.75(14)\\ 168.19(12)\\ 80.36(13)\\ 99.71(12)\\ 80.87(13)\\ 98.46(12)\\ 161.21(13)\\ 173.86(13)\\ 80.08(16)\\ 98.16(13)\\ 81.17(16)\\ 99.94(13)\\ 160.54(14) \end{array}$	
Cu1–N1 Cu1–N2 Cu1–N3 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.975(3) 1.949(3) 1.947(4) 1.931(3) 1.942(3) 1.942(3) 1.942(3)	Ac)}DMF	N4O1 N6O1 H4O1 H6O1 N10O2 H10O2 H10O2 H10O2 H12O2 H10O3 N18O3 H16O3 H16O3 H18O3	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421 3.090(5) 2.984(4) 2.503 2.398	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N1 N2-Cu1-N3 O1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-O3 N14-Cu3-N13 O3-Cu3-N15 N13-Cu3-N15	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.08(16) 98.16(13) 81.17(16) 99.94(13) 160.54(14)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.975(3) 1.945(3) 1.975(3) 1.949(3) 1.947(4) 1.931(3) 1.942(3) 2L5)Cu(O 2.005(2)	Ac)}DMF	N4O1 N6O1 H4O1 H6O1 N10O2 H10O2 H10O2 H10O2 H12O2 H10O3 N18O3 H16O3 H16O3 H18O3 H1	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421 3.090(5) 2.984(4) 2.503 2.398 3.096(5)	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N1 N2-Cu1-N3 O1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-O1 N14-Cu3-N13 O3-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.08(16) 98.16(13) 81.17(16) 99.94(13) 160.54(14) 177.84(6)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.923(3) 1.991(3) 1.945(3) 1.945(3) 1.975(3) 1.949(3) 1.947(4) 1.931(3) 1.942(3) 2L5)Cu(O 2.005(2) 1.915(2)	Ac)}·DMF	N4O1 N6O1 H4O1 H6O1 N10O2 H10O2 H10O2 H10O2 H10O2 H10O2 H10O2 H10O3 H10O3 H16O3 H16O3 H16O3 H18O3 H1	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.420 2.984(4) 2.503 2.398 3.090(5) 3.096(5) 3.164(3)	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N7-Cu2-N9 N14-Cu3-O3 N14-Cu3-N13 O3-Cu3-N13 N14-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.17(16) 99.94(13) 160.54(14) 177.84(6) 80.55(6)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu1–O1 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.919(3) 1.919(3) 1.9475(3) 1.949(3) 1.949(3) 1.949(3) 1.949(3) 1.942(3) 2.042(2) 2.005(2) 1.915(2) 2.018(2)	Ac)] ⁻ DMF	N4O1 N6O1 H4O1 H6O1 N10O2 N12O2 H10O2 H10O2 H10O2 H10O3 N18O3 H16O3 H16O3 H18O3 H18O3 H18O7 N5O7 H4O7	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421 3.090(5) 2.984(4) 2.984(4) 2.503 2.398 3.096(5) 3.164(3) 2.183	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-N13 O3-Cu3-N13 N14-Cu3-N15 N14-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.16(13) 81.17(16) 99.94(13) 160.54(14) 177.84(6) 80.55(6) 100.68(6)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu2–N7 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.979(3) 1.975(3) 1.949(3) 1.949(3) 1.949(3) 1.949(3) 1.942(3) 2.052(4) 2.05(2) 1.915(2) 2.018(2) 1.912(1)	Ac)}DMF	N4O1 N6O1 H4O1 H6O2 N10O2 H10O2 H12O2 H12O2 H12O2 H12O2 H12O3 N18O3 H16O3 H18O3 H18O3 H18O7 H4O7 H4O7 H5O7	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421 3.090(5) 2.984(4) 2.503 2.398 2.398 3.096(5) 3.164(3) 2.183 2.691	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-N13 O3-Cu3-N13 N14-Cu3-N15 O3-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N2-Cu1-O1 N2-Cu1-N1 N2-Cu1-N3	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.08(16) 98.16(13) 81.17(16) 99.94(13) 160.54(14) 177.84(6) 80.55(6) 100.68(6) 81.00(7)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.923(3) 1.945(3) 1.945(3) 1.979(3) 1.919(3) 1.949(3) 1.949(3) 1.949(3) 1.949(3) 1.949(3) 1.942(3) 2.015(2) 2.018(2) 1.912(1) 2.819(2)	Ac)}·DMF	N4O1 N6O1 H4O1 H6O1 N10O2 H10O2 H12O2 H12O2 H12O2 H12O2 H12O2 H12O2 H12O2 H12O2 H12O3 H18O7 H3O7 H3O7 H3O7	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421 3.090(5) 2.984(4) 2.503 2.398 3.095(5) 3.164(3) 2.183 2.691	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-N3 N8-Cu2-N7 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N14-Cu3-N13 O3-Cu3-N13 N14-Cu3-N15 N13	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.08(16) 98.16(13) 81.17(16) 99.94(13) 160.54(14) 177.84(6) 80.55(6) 100.68(6) 81.00(7) 97.65(6)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu1–O1 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.979(3) 1.9475(3) 1.9475(3) 1.9476(4) 1.947(4) 1.942(3) 2.005(2) 1.917(4) 2.005(2) 1.915(2) 2.018(2) 1.912(1) 2.819(2)	Ac)}DMF	N4O1 N6O1 H4O1 H6O1 N10O2 N12O2 H10O2 H10O2 H10O2 H10O2 H10O3 N18O3 H16O3 H16O3 H16O3 H18O3 H18O7 N5O7 H4O7 H5O7	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.420 2.984(4) 2.984(4) 2.984(4) 2.503 2.398 3.096(5) 3.164(3) 2.183 2.691	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-03 N14-Cu3-N13 O3-Cu3-N13 N14-Cu3-N15 N13-Cu	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.16(13) 81.17(16) 99.94(13) 160.54(14) 177.84(6) 80.55(6) 100.68(6) 81.00(7) 97.65(6) 161.14(7)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3 [NMe₄][(H] Cu1–N1 Cu1–N2 Cu1–N3 Cu1–O1 Cu1–O2	1.979(3) 1.923(3) 1.923(3) 1.945(3) 1.919(3) 1.919(3) 1.975(3) 1.949(3) 1.945(3) 1.949(3) 1.949(3) 1.9442(3) 2.045(2) 1.942(3) 2.005(2) 1.915(2) 2.018(2) 1.912(1) 2.819(2) 2.05(CuC]	Ac)}DMF	N4O1 N6O1 H4O1 H6O1 N10O2 H10O2 H12O2 H12O2 H12O2 H12O2 H12O2 H12O3 N18O3 H18O3 H18O3 H18O3 H18O3 H18O7 N5O7 H4O7 H4O7 H5O7	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421 3.090(5) 2.984(4) 2.503 2.398 3.096(5) 3.164(3) 2.183 2.691	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N1 N2-Cu1-N3 O1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 N8-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-O3 N14-Cu3-N13 O3-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu1-N1 N2-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.08(16) 98.16(13) 81.17(16) 99.94(13) 160.54(14) 177.84(6) 80.55(6) 100.68(6) 81.00(7) 97.65(6) 161.14(7)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.923(3) 1.991(3) 1.945(3) 1.979(3) 1.975(3) 1.949(3) 1.975(3) 1.949(3) 1.937(4) 1.931(3) 1.977(4) 1.942(3) 2.005(2) 1.915(2) 2.018(2) 1.912(1) 2.819(2) 2.043(Ac)}DMF	N4O1 N6O1 H4O1 H6O1 N10O2 H12O2 H12O2 H12O2 H12O2 H12O2 H12O2 N18O3 H18O3 H18O3 H18O3 H18O3 H18O3 H18O3 H18O7 N5O7 H4O7 N5O7 H4O7 H5O7	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421 3.090(5) 2.984(4) 2.503 2.398 3.096(5) 3.164(3) 2.183 2.691	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N1 N2-Cu1-N3 O1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-O3 N14-Cu3-N13 O3-Cu3-N13 N14-Cu3-N15 N13-Cu3-N15 N12-Cu1-N3 N1-Cu1-N3 N1-Cu1-N3	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.74(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.08(16) 98.16(13) 81.17(16) 99.94(13) 160.54(14) 177.84(6) 80.55(6) 100.68(6) 81.00(7) 97.65(6) 161.14(7)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu1–O1 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.923(3) 1.945(3) 1.945(3) 1.919(3) 1.975(3) 1.949(3) 1.949(3) 1.937(4) 1.937(4) 1.937(4) 1.942(3) 2.005(2) 1.915(2) 2.018(2) 1.912(1) 2.819(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(2) 1.912(2) 2.043(Ac)]·DMF	N4O1 N6O1 H4O1 H6O1 N10O2 N12O2 H10O2 H10O2 H10O2 H10O2 N12O2 H10O3 N18O3 H16O3 H1	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.421 3.090(5) 2.984(4) 2.503 2.398 3.096(5) 3.164(3) 2.183 2.691 3.348(3) 4.013(3) 2.021	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N7-Cu2-N9 N14-Cu3-N13 O3-Cu3-N13 N14-Cu3-N13 O3-Cu3-N15 N13-Cu3-	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.08(16) 98.16(13) 81.17(16) 99.94(13) 160.54(14) 177.84(6) 80.55(6) 100.68(6) 81.00(7) 97.65(6) 161.14(7) 178.05(5) 80.56(7) 80.56(7)	
Cul–N1 Cul–N2 Cul–N3 Cul–O1 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.921(3) 1.945(3) 1.979(3) 1.919(3) 1.919(3) 1.9475(3) 1.9475(3) 1.9476(4) 1.942(3) 2.018(2) 2.018(2) 1.912(1) 2.819(2) 2.043(2) 1.918(2) 2.043(2) 1.918(2) 2.012(2) 2.0	Ac)}DMF	N4O1 N6O1 H4O1 H6O1 N10O2 N12O2 H10O2 H10O2 H10O2 H10O2 H10O2 H10O3 N18O3 H16O3 H16O3 H16O3 H18O3 H18O3 H18O7 H5O7 H4O7 H5O7 H4O7 H5O7	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.421 2.984(4) 2.984(4) 2.984(4) 2.984(4) 2.984(4) 2.984(4) 2.503 2.398 3.164(3) 2.183 2.691 3.348(3) 4.013(3) 2.602	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N7-Cu2-N9 N14-Cu3-03 N14-Cu3-N13 O3-Cu3-N13 N14-Cu3-N15 O3-Cu3-N15 N12-Cu1-N1 N1-Cu1-N3 N1-Cu1-N1 N2-Cu1-C11 N2-Cu1-N1 C11-Cu1-N1 C11-Cu1-N1 N2-Cu1-N1 C11-Cu1-N1	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.08(16) 98.16(13) 81.17(16) 99.94(13) 160.54(14) 177.84(6) 80.55(6) 100.68(6) 81.00(7) 97.65(6) 161.14(7) 178.05(5) 80.56(7) 99.81(5) 80.55(7)	
Cul–NI Cul–N2 Cul–N3 Cul–OI Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.923(3) 1.945(3) 1.945(3) 1.979(3) 1.919(3) 1.947(3) 1.949(3) 1.949(3) 1.949(3) 1.942(3) 2.042(3) 2.018(2) 2.043(2) 1.918(2) 2.021(2) 2.1852(5)	Ac)]-DMF -CH3CN (9	N4O1 N6O1 H4O1 H6O1 N10O2 N12O2 H10O2 H10O2 H12O2 N16O3 N18O3 H16O3 H16O3 H18O3 H18O3 H18O3 H18O7 H5O7 H5O7 H5O7 H5O7 H5O7 H5N6 H4N6 H5N6	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.421 3.090(5) 2.984(4) 2.430 2.2503 2.398 3.090(5) 3.164(3) 2.183 2.691 3.348(3) 4.013(3) 2.602 2.628	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-N13 O3-Cu3-N13 O3-Cu3-N13 N14-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N12-Cu1-N1 O1-Cu1-N3 N1-Cu1-N3 N1-Cu1-N3 N1-Cu1-N3 N1-Cu1-N3 N1-Cu1-N1 N2-Cu1-N1 Cl1-Cu1-N1 N2-Cu1-N1 Cl1-Cu1-N1 N2-Cu1-N1 N2-Cu1-N1 Cl1-Cu1-N1 N2-Cu1-N1 N1-Cu1-N1 N2-Cu1-N1 N1-Cu1-N1 N2-Cu1-N1 N1-Cu1-N1 N2-Cu1-N1 N1-Cu1-N1 N2-Cu1-N1 N1-Cu1-N1 N2-Cu1-N1 N1-Cu1-N1 N2-Cu1-N1 N1-Cu1	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 98.46(12) 161.21(13) 173.86(13) 80.16(13) 81.17(16) 99.94(13) 160.54(14) 177.84(6) 80.55(6) 100.68(6) 81.00(7) 97.65(6) 161.14(7) 178.05(5) 80.23(6) 80.23(6) 80.23(6)	
Cu1–N1 Cu1–N2 Cu1–N3 Cu2–N7 Cu2–N8 Cu2–N9 Cu2–O2 Cu3–N13 Cu3–N14 Cu3–N15 Cu3–O3	1.979(3) 1.923(3) 1.923(3) 1.945(3) 1.945(3) 1.979(3) 1.975(3) 1.949(3) 1.949(3) 1.945(3) 1.949(3) 1.942(3) 2.042(3) 2.015(2) 2.018(2) 2.018(2) 2.043(2) 1.918(2) 2.021(2) 2.1852(5)	Ac)}DMF 'CH3CN (9	N4O1 N6O1 H4O1 H6O1 N10O2 H12O2 H12O2 H12O2 H12O2 H12O2 H12O3 H16O3 H16O3 H16O3 H18O3 H18O3 H18O3 H18O7 H5O7 H4O7 H5O7 H4O7 H5O7 H5N6 H4N6 H5N6	3.045(4) 3.167(4) 2.219 2.395 3.108(4) 3.140(4) 2.440 2.421 3.090(5) 2.984(4) 2.984(4) 2.984(4) 2.984(4) 2.503 2.398 3.096(5) 3.164(3) 2.183 2.691 3.348(3) 4.013(3) 2.602 2.628	N2-Cu1-O1 N2-Cu1-N1 O1-Cu1-N3 O1-Cu1-N3 N1-Cu1-N3 N8-Cu2-O2 N8-Cu2-N7 O2-Cu2-N7 N8-Cu2-N9 O2-Cu2-N9 N7-Cu2-N9 N14-Cu3-N13 O3-Cu3-N13 N14-Cu3-N13 O3-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu3-N15 N13-Cu1-N1 N2-Cu1-N1 N2-Cu1-N1 N2-Cu1-N1 N2-Cu1-N1 N2-Cu1-N3 Cl1-Cu1	171.37(12) 80.68(14) 100.31(12) 80.35(14) 97.95(12) 160.75(14) 168.19(12) 80.36(13) 99.71(12) 80.87(13) 99.846(12) 161.21(13) 173.86(13) 80.08(16) 98.16(13) 81.17(16) 99.94(13) 160.54(14) 177.84(6) 80.55(6) 100.68(6) 81.00(7) 97.65(6) 161.14(7) 178.05(5) 80.23(6) 99.81(5) 80.23(6) 99.82(5)	

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 (in 3), acetate (in 4), or hydroxide (in 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 is 2.202 Å, O1…H6 is 2.197 Å, O1…N4 is 3.003(2) Å, and O1····N6 is 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 those in analogous systems without hydrogen bonding, as in the case for 1b compared to 5, for which the Cu-OH distances are 1.863 and 1.884 Å, respectively.^[8] Beyond the elongation of the Cu-X distances, the geometry around the Cu^{II} center is nearly identical to those of non-hydrogen-bonded systems. The retention of the indicated overall formulations for the complexes in solution was indicated by EPR spectroscopy (for compounds 3-5) and negative-ion-mode ESI-MS (for compounds 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 hydrogen bonding patterns were observed in the products of CO_2 fixation by the hydroxide complex 5. Thus, exposure of solutions of 5 in DMF to air followed by diffusion of Et₂O led to the formation of purple crystals, which were identified as a mixture of $[NMe_4]_2[{(H_2L4)}]$ $Cu_{2}(CO_{3})$ (6) and $[NMe_{4}]_{2}[\{(H_{2}L4)Cu_{3}(CO_{3})\}]$ (7) on the basis of X-ray crystallography and ESI-MS (7; Figure S5) performed on crystals selected randomly from the batch (Figures 3 and 4, Table 1). In both complexes, $[(H_2L4)Cu]$ units surround a carbonate ion. In 6, two such units are present, and the Cu^{II}–O3 distance [2.5425(3) Å] is longer than that for the equatorial O1 [1.9602(2) Å]. This type of coordination mode has been observed 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 group 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 η^1 fashion, a precedented tricopper-carbonate motif.^[15] Again, intramolecular hydrogen bonding 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 of the hydrogen bonding interactions on the reactivity of 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 observed for [(L2)CuOH]⁻ ($i_{pc}/i_{pa} \approx 1$, $E_{1/2}$ =





Figure 3. (a) Representation of the anionic portion of the X-ray structure of $[NMe_4]_2[\{(H_2L4)Cu\}_2(CO_3)]$ (6), showing all non-hydrogen atoms as 50% thermal ellipsoids and hypothesized hydrogen bonds as dashed lines. (b) Expanded view of the core, with all carbon atoms (except C36) omitted.

-67 mV vs. Fc⁺/Fc, $\Delta E_p = 134 \text{ mV}$) similar to that 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 about 350 mV higher than that for [(L2)CuOH]⁻. Similarly, reversibility is greater for [(L2) CuCl⁻ (Figure 5b) than that for 3, which shows only a small reverse scan wave at high scan rates, and the approximated $E_{1/2}$ for **3** is about 300 mV higher than that for [(L2) CuCl]-. The significant redox potential increases for 3 and 5 relative to the complexes of $L2^{2-}$ are similar to those reported previously for systems having analogous secondarysphere 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 H_2L4^{2-} and $L2^{2-}$ 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 $L3^{4-}$, we targeted complexes of ligand H_2L5^{2-} .



Figure 4. (a) Representation of the anionic portion of the X-ray structure of $[NMe_4]_2[\{(H_2L4)Cu\}_3(CO_3)]$ (7), showing all non-hydrogen atoms as 50% thermal ellipsoids and hypothesized hydrogen bonds as dashed lines. (b) Expanded view of the core, with all carbon atoms (except C63) omitted.



Figure 5. Cyclic voltammograms (0.1 M Bu₄NPF₆, Pt electrode) of (a) the complexes (i) [(**L2**)CuOH]⁻ and (ii) [(H₂**L4**)CuOH]⁻ (**5**) in DMA, and (b) the complexes (iii) [(**L2**)CuCl]⁻, (iv) [(H₂**L4**)CuCl]⁻ (**3**), and (v) [(H₂**L5**)CuCl]⁻ (**9**, R' = *t*Bu) in CH₃CN. 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.



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

Compound	Solvent	$E_{1/2} [\text{mV}]^{[b]}$
[(L2)CuOH] ⁻	DMA	-67
$[(H_2L4)CuOH]^-$ (5)	DMA	+284
[(L2)CuCl]	CH ₃ CN	+338
$[(H_2L4)CuCl]^-$ (3)	CH ₃ CN	+632
$[(H_2L5)CuCl]^-$ (9)	CH ₃ CN	+581

[a] Conditions: room temperature, $0.1 \text{ M Bu}_4\text{NPF}_6$. [b] Potentials measured with a Pt electrode vs. Fc⁺/Fc.

Complexes of H₂L5²⁻

Reported syntheses of macrocycle H_4L5 (R = H) and related macrocycles involve ring-closing condensations of a hemicycle precursor, N², N⁶-bis(2-aminophenyl)pyridine-2,6-dicarboxamide.^[16] Using a procedure similar to one previously described, H₄L5 was synthesized from the hemicycle by condensation with the corresponding isophthalic dichloride (R = H or tBu; Scheme 2). Treatment of H_4L5 $(\mathbf{R}' = \mathbf{H} \text{ or } t\mathbf{B}\mathbf{u})$ with NMe₄OH (2 equiv.) followed by CuX₂ (X = OAc or Cl) yielded monocopper complexes 8 (R' = H) or 9 (R' = tBu), respectively, the formulations of which were determined on the basis of EPR spectroscopy, highresolution 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 Xray crystal structures of these complexes revealed hydrogen bonding from the free carboxamide N-H groups to the solvate molecules (8: DMF, the source of which is unclear; 9: CH₃CN), but no hydrogen bonds were observed to the



Scheme 2. Synthesis of H₄L5 and complexes 8 and 9. (i) NEt₃, THF. (ii) (a) CF₃CO₂H (b) NaOH (c) isophthalic or 5-*tert*-butyl-isophthalic dichloride, NEt₃, THF. (iii) NMe₄OH (2 equiv.), CuX₂ (X = Cl or OAc), S.

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 [(L2)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 $E_{1/2} = +581 \text{ mV}$ vs. Fc⁺/Fc (Figure 5b, v), which is about 240 mV greater than that of [(L2)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 a Cu^{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 observed in the X-ray structures of 3-7. Attempts to analyze these complexes in a non-hydrogenbond-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



Figure 6. (a) Representations of the anionic portion of the X-ray structures of (a) $[NMe_4][(H_2L5)Cu(OAc)]$ ·DMF (8, R' = H) and (b) $[NMe_4][(H_2L5)CuCl]$ ·CH₃CN (9, R' = tBu), showing all non-hydrogen atoms as 50% thermal ellipsoids and hypothesized hydrogen bonds as dashed lines.



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 Cu^{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 L3⁴⁻, which forms dicopper complexes, treatment of H₄L4 with base and Cu^{II} salts results in the formation of complexes in which H_2L4^{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 CO₃²⁻) bound to the Cu^{II} ion. These secondary coordination sphere hydrogen bonding interactions result in significant positive shifts in the Cu^{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 monocopper complex 9 supported by the purposefully mononucleating ligand H_2L5^{2-} that features aryl groups on the carboxamido donors. While the Xray 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 by using Schlenk techniques or a glove box unless otherwise noted. HPLC grade water was distilled and degassed by one freeze-pump-thaw cycle. Solvents tetrahydrofuran (THF), diethyl ether (Et₂O), pentane, and dichloromethane (CH₂Cl₂) were passed through solvent purification columns (Glass Contour, Laguna, CA). Pyridine and ethylenediamine 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 with a Bruker Elexsys E500 spectrometer. Simulations were performed with Bruker SimFonia software (version 1.25). Electrospray ionization mass spectrometry (ESI-MS) was performed with a Bruker Bio-TOF II instrument. Cyclic voltammetry (CV) was performed in a three-electrode cell with a 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 by using Schlenk line techniques. 6-Pyridinedicarboxylic 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

ethylenediamine (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 through 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 \times 50 mL), a solution of NaHCO₃ (0.1 m, 2 \times 200 mL), a solution of K_2CO_3 (0.1 M, 2 × 200 mL), and a solution of NaOH (0.1 m, 2×200 mL). MeOH (40 mL) was added to the washed product, and the mixture was heated at reflux for 40 min and cooled; the solid was collected by filtration with a Büchner funnel. After being washed with additional MeOH $(2 \times 30 \text{ mL})$ and Et₂O (2 \times 30 mL), the white solid was allowed to dry in air. This white solid was then heated at reflux once more with DMF (180 mL) for 10 min, filtered while hot, and the filtrate was cooled to room temperature, producing white crystals of H₄L4 (yield: 9.04 g, 40%). ¹H NMR ([D₆]DMSO, 300 MHz): δ = 9.46 (s, 4 H, NHCO), 8.24-8.17 (m, 6 H, CHPy), 3.61-3.60 (m, 8 H, CH₂) ppm. C₁₈H₁₈N₆O₄ (382.38): calcd. 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 by 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 were added Et₂O (20 mL) and hexanes (20 mL), and a white solid was filtered off with a 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 concentration of the filtrate over 2 d. The white crystals were collected by filtration, washed with hexane $(2 \times 10 \text{ mL})$, and dried in air (yield: 21.9 g, 70.4%). The ¹H NMR spectrum matched those reported.^[16,17] This compound was carried on as a precursor for the synthesis of the hemicycle, N², N⁶-bis(2-aminophenyl)pyridine-2,6dicarboxamide.

 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-1,2phenylenediamine (10.41 g, 0.050 mol) and NEt₃ (10 mL) 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 Et_2O (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 (2 M, 500 mL). The solution was immersed in an ice bath and cooled. Additional CH₂Cl₂ (ca. 900 mL) was added to dissolve the entire product, and the CH₂Cl₂ layer was washed with water (3× 200 mL), dried with Na₂SO₄, and volatiles removed under vacuum to afford a yellow solid. Recrystallization of this yellow solid from CH₂Cl₂ (100 mL) and Et2O (100 mL) at 0 °C yielded pure compound 5 (yield: 8.68 g, 80%). The ¹H NMR spectrum matched those reported.[16,17]

 H_4L5 (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 an argon atmosphere. The mixture was cooled to room temperature, left to stir for an additional 24 h, filtered, and the solvent was removed from the filtrate under vacuum to give a sticky brown solid. Addition of MeOH (300 mL) generated a white suspension, which was filtered. The filtrate was collected and concentrated to about 50 mL. Et₂O (50 mL) was added to give a white powder that was collected by filtration and then washed with Et_2O (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 h to yield the product, which was dried under vacuum (yield: 0.94 g, 68%). ¹H NMR ([D₆]DMSO, 300 MHz): δ = 11.15 (s, 2 H, NHCO), 10.21 (s, 2 H, NHCO), 9.28 (s, 1 H, CH), 8.43–8.40 (d, 2 H, CH^{Py}), 8.29–8.24 (m, 1 H, CH^{Py}), 8.15-8.07 (m, 4 H, CH), 7.72-7.66 (m, 2 H, CH), 7.37-7.25 (m, 4 H, CH) ppm. $C_{30}H_{26}N_6O_5$ [550.56; H_4L5 (R' = H) with one molecule of DMF]: calcd. C 65.45, H 4.76, N 15.26; found C 64.57, H 4.70, N 15.32.

H₄**L5** (**R**' = *t***Bu**): This compound was synthesized analogously to H₄**L5** (**R**' = H), but 5-*tert*-butyl-isophthalic dichloride was used instead of isophthalic dichloride (yield: 1.85 g, 60.2%). ¹H NMR ([D₆]DMSO, 300 MHz): δ = 11.25 (s, 2 H, NHCO), 10.30 (s, 2 H, NHCO), 9.22 (s, 1 H, CH), 8.42–8.39 (d, 2 H, CH^{Py}), 8.28–8.22 (m, 1 H, CH^{Py}), 8.10–8.04 (m, 4 H, CH), 7.68–7.65 (m, 2 H, CH), 7.36–7.26 (m, 4 H, CH), 1.33 (s, 9 H, CH₃) ppm. C₃₄H₃₄N₆O₅ [606.67; H₄L5 (**R**' = *t*Bu) with one molecule of DMF]: calcd. 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 the solution to stir for 12 h, the solvent was removed under vacuum, and the resulting purple powder was dissolved in DMF (5 mL). Diffusion of Et₂O vapor into the solution afforded the product as purple crystals, which were dried under vacuum (yield: 0.236 g, 58%). HR-MS (ESI, CH₃OH): calcd. for $[3 - NMe_4^+]^-$ 478.022; found 478.137. C₂₂H₂₈ClCuN₇O₄ (553.50): calcd. 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, but Cu(OAc)₂·H₂O was used instead of CuCl₂ (yield: 0.187 g, 42%). HR-MS (ESI, CH₃OH): calcd. for $[4 - NMe_4^+]^-$ 502.066; found 502.032. C₂₄H₃₁CuN₇O₆ (577.09): calcd. C 49.95, H 5.41, N 16.99; found C 49.26, H 5.59, N 16.74.

 $[NMe_4][(H_2L4)Cu(OH)]$ (5): Compound H_4L4 (300 mg, 0.78 mmol) was added to a degassed solution of 1:3 water/pyridine. Subsequently, a NMe₄OH solution in water (2.18 M, 0.55 mL, 0.0025 mol) was added to this solution, which resulted in a yellow color. An equivalent of Cu(OTf)₂ (281 mg, 0.78 mmol) was added slowly to the solution, which resulted in a slight green color that turned purple after stirring for several minutes. The solution was left to stir for 12 h, 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. The mixture was placed in a vial and kept under a nitrogen atmosphere at room temperature. After 5 d, purple crystals were observed on the sides of the vial, which were found to be 5 (yield: 53 mg, 12%). C₂₂H₂₉CuN7O5 (535.06): calcd. C 49.39, H 5.46, N 18.32; found C 49.05, H 5.93, N 17.97.

 $(NMe_4)_2[(H_2L4Cu)_2CO_3]$ (6) and $(NMe_4)_2[(H_2L4Cu)_3CO_3]$ (7): Compound 5 (200 mg, 0.40 mmol) was dissolved in DMF (10 mL), and the solution was left open to atmospheric CO₂ for over 24 h. Upon diffusion of Et₂O vapor into the DMF solution, purple crystals were isolated and identified as a mixture of 6 and 7 by Xray crystal structures of randomly selected crystals. An ESI-mass spectrum of one crystal was consistent with 7. ESI-MS (CH₃OH): calcd. for $[7 - 2 NMe_4^+]^{2-}$ 695.571; found 695.754. 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 was added a NMe₄OH solution in MeOH (2.18 M, 0.13 mL, 0.6 mmol), and the solution was left to stir for 10 min., which resulted in a clear yellow solution. To this yellow solution was added an equivalent of dry CuCl₂ (40 mg, 0.3 mmol), which resulted in a color change of the solution to green. The reaction was left to stir at room temperature for 2 h, the solution was filtered, and the solvent was removed to afford a green powder. The powder was dissolved in acetone (10 mL), filtered, and the solvent was removed to afford 9 (yield: 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): calcd. for [9 – NMe₄+]⁻ 630.568; found 631.134. 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, but Cu(OAc)₂·H₂O was used instead of CuCl₂ (yield: 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): calcd. for $[8 - NMe_4^+]^-$ 597.071; found 597.136. 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 by using Mo- K_{α} or Cu- K_{α} radiation with a graphite monochromator (λ = 0.71073 or 1.54184 Å) at 173 or 123 K, respectively. Structure solutions were performed by direct methods with SHELXS-2013 software^[18] and refined against F^2 with full-matrix-least-squares by using SHELXL-97^[18] and SHELXL-2013 software.^[19] 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 $U_{eq} = 1/3(U_{11}+U_{22}+U_{33})$. 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.

CCDC-1424005 (for 7), -1424006 (for 6), -1424007 (for 3), -1424008 (for 4), -1424009 (for 5), -1424010 (for 8), -1424011 (for 9) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): NMR, EPR, and ESI-MS spectra.



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