Multinuclear copper complexes of pyridylmethylamide ligands

Urmila Pal Chaudhuri, Laura R. Whiteaker, Lei Yang and Robert P. Houser*

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Copper complexes of a family of pyridylmethylamide ligands HL^{Ph} , HL^{Me3} and HL^{Ph3} were synthesized and characterized [$HL^{Ph} = 2$ -phenyl-*N*-(2-pyridylmethyl)acetamide; $HL^{Me3} = 2,2$ -dimethyl-*N*-(2-pyridylmethyl)propionamide; $HL^{Ph3} = 2,2,2$ -triphenyl-*N*-(2-pyridylmethyl)acetamide]. The reaction of copper(II) salts with the HL family and triethylamine in methanol yields copper(II) complexes [$Cu_4(L^{Ph})_4(OH)_2$]($ClO_4)_2$ (1), [$Cu_2(HL^{Me3})_2(OMe)_2(MeOH)_2$]($OTf)_2$ (2) and [$Cu_2(HL^{Ph3})_2(OMe)_2$ -($MeOH)_2$]($OTf)_2$ (3). The complexes have different nuclearity owing to varying steric properties of the ligands used. Complex 1 self-assembles in the presence of excess base to form a tetranuclear complex. Complexes 2 and 3 are binuclear and are bridged by a pair of methoxide ligands. Steric encumbrance of the ligands in 2 and 3 prevent cluster formation.

Introduction

Polynuclear copper complexes have been studied extensively due to their ability to function as new nanometric materials and single-molecule magnets.¹ In addition, they can model structural and functional aspects of several multicopper active sites of metalloproteins.² The metal centers are often bridged by hydroxo, alkoxo or azido groups mediating magnetic exchange and feature prominently in magnetochemical studies aimed at developing correlations between molecular structure and magnetic behavior. Hydroxo- and alkoxo-bridged metal complexes exhibit magnetic behavior ranging from ferromagnetic to antiferromagnetic depending on the geometry of the $Cu_2(OR)_2$ (R = H, alkyl, aryl) bridging units. Studies have established that the type and magnitude of interaction is influenced by the Cu ··· Cu separation, Cu–O (bridge) distance, the Cu–O–Cu angle (θ) , the dihedral angle between the planes formed by the two adjoining CuO units in a Cu_2O_2 core, and the Cu(II) center geometry.³ Interestingly, these polynuclear complexes, generally formed by self-assembly, display unique structural features that are susceptible to change upon minor variation of ligand structure and reaction conditions.

Previously, we reported the structural properties of an octanuclear copper(II) complex $[Cu_8L_8(OH)_4](ClO_4)_4$ [HL = *N*-(2pyridylmethyl)acetamide] which self-assembles from the reaction of copper(II) perchlorate, HL and Et₃N in methanol.⁴ The structure of $[Cu_8L_8(OH)_4](ClO_4)_4$ consists of two pseudosymmetric tetracopper clusters that are held together by bridging ligands and hydrogen bonding. Each tetranuclear half of the full cluster contains four copper ions, four ligands, and two μ_3 -hydroxo ligands. We have probed this chemistry further by synthesizing a family of ligands derived from the basic *N*-(2-pyridyl)acetamide (HL) backbone, and have observed the formation of different core structures under varying reaction conditions. Herein, we present the syntheses of ligands HL^{Ph} , HL^{Me3} and HL^{Ph3} [HL^{Ph} = 2-phenyl-*N*-(2-pyridylmethyl)acetamide; $HL^{Ph3} = 2,2$ -dimethyl-*N*-(2-pyridylmethyl)propionamide; $HL^{Ph3} = 2,2$ -triphenyl-*N*- (2-pyridylmethyl)acetamide] and their copper complexes $[Cu_4-(L^{Ph})_4(OH)_2](ClO_4)_2$ (1), $[Cu_2(HL^{Me3})_2(OMe)_2(MeOH)_2](OTf)_2$ (2), and $[Cu_2(HL^{Ph3})_2(OMe)_2(MeOH)_2](OTf)_2$ (3). Complexes 1–3 represent interesting variations in core structures due to the structural differences of the ligands.

Results and discussion

Syntheses and characterization

Our ligand design and synthesis originate from an earlier report from our laboratory where copper(II) clusters were synthesized using the ligand *N*-(2-pyridylmethyl)acetamide (HL).⁴ HL was synthesized *via* a simple procedure whereby 2-aminomethyl pyridine reacts with acetic anhydride.⁵ The related ligand 2-methylthio-*N*-(2-pyridylmethyl)acetamide (HL^{SMe}) was synthesized in our lab *via* the DCC-mediated coupling of methylthioacetic acid with 2aminomethyl pyridine.⁶ In view of the interesting coordination chemistry generated by HL and HL^{SMe} with copper, we targeted other derivatives of HL and obtained a versatile family of pyridyl amide ligands using either direct coupling methods or activating agents.

Ligand synthesis

Functionalized derivatives of HL, namely HL^{Ph} and HL^{Me3} (Scheme 1), were synthesized using the direct synthetic route whereby the respective acid chloride was treated with 2-aminomethyl pyridine in the presence of triethylamine at 0 °C. The solutions were stirred for 24 h followed by a basic workup producing the ligands in high yields. The steric bulk and electron-withdrawing nature of the additional phenyl groups in HL^{Ph3} deactivates the amine from undergoing condensation when triphenylacetic acid was reacted with 2-aminomethyl pyridine as outlined above, so it was necessary to use a coupling agent. Therefore, HL^{Ph3} was synthesized using triphenylacetic acid in the presence of triethylamine in DMF, and Py-BOP was used as the coupling reagent to activate the acid to form the corresponding activated ester (Scheme 1). Trial reactions with DCC/HOBt were also carried out but did not drive the reaction to completion,

Department of Chemistry and Biochemistry, University of Oklahoma, 620 Parrington Oval, Norman, Oklahoma, 73019, USA. E-mail: houser@ ou.edu; Fax: (405) 325-6111; Tel: (405) 325-3551



so Py-BOP was used with maximum efficiency. All ligands were characterized by elemental analysis, FTIR, and ¹H NMR.

Copper complexes

Copper complexes of HL^{Ph}, HL^{Me3} and HL^{Ph3} were synthesized in methanol by reaction of cupric salts with the respective ligands in the presence of triethylamine. Previously we reported the synthesis and characterization of octanuclear copper clusters utilizing N-(2-pyridylmethyl)acetamide (HL).⁴ The unusual chemistry of HL lies in the versatility through which it coordinates to the copper(II) ions. Complexes with HL in the neutral form are simple mononuclear species where the ligand coordinates in a bidentate fashion via the pyridyl N atom and the amido O atom.⁴ When the amide nitrogen is deprotonated, the anionic amidate ligand forms octanuclear clusters and the anionic amidate ligand (L⁻) coordinates via three atoms in a bridging fashion. The N atoms from the pyridyl group and the amidate chelate one copper ion and the amidate O atom coordinates to a second copper ion. Along with four bridging hydroxo ligands, eight ligands combine with eight copper ions to form an octanuclear cluster.⁴ A similar synthetic trend was observed with HL^{Ph}.

In the absence of a base, the pyridylmethylamide ligands remain in the neutral form and exclusively produce mononuclear copper complexes.^{4,7} However, a base is crucial for the generation of the anionic form of the ligand (L^{ph-}) as observed in the copper cluster [Cu₄(L^{Ph})₄(OH)₂](ClO₄)₂ (1, Scheme 2). Furthermore, a base is absolutely essential for the formation of the hydroxide bridging ions by deprotonation of water, presumably from the $Cu(ClO_4)_2 \cdot 6H_2O$ starting material. In order to understand the stoichiometry and the exact role of the base, we carried out the reaction using different ratios of triethylamine. We observed that there was no isolable cluster when one equivalent of triethylamine was used, but an uncharacterized blue oil forms. However, the use of slight excess of triethylamine resulted in the formation of the hydroxide bridged cluster, 1. Optimal yields were obtained when 1.5 equivalents of triethylamine was added for every one equivalent of ligand used. Hence, to synthesize the cluster containing four ligands, a total of six equivalents of triethylamine was used. Four



Scheme 2 Complexes 1–3.

of these equivalents generate the amidate form of L^{ph-} and the remaining two equivalents deprotonate two waters forming the μ_3 -hydroxo ligands. Reactions were also carried out using two equivalents of triethylamine for every one equivalent of the ligand used, but in this case 1 did not form and an uncharacterized insoluble blue copper species resulted.

Interestingly, when triethylamine was used to deprotonate the amide nitrogen in HL^{Me3} and HL^{Ph3} , it deprotonated the solvent methanol and formed isostructural methoxide bridged clusters [Cu₂(HL^{Me3})₂(OMe)₂(MeOH)₂](OTf)₂ (2) and $[Cu_2(HL^{Ph3})_2(OMe)_2(MeOH)_2](OTf)_2$ (3). When the same reaction was performed in acetonitrile with just one equivalent of triethylamine, the solution turned turbid and deposited an insoluble precipitate characterized as copper hydroxide. The same phenomenon was observed when 1.5 or more equivalents of triethylamine was used. The formation of copper hydroxide was indicated by the presence of the OH band ($v = 3438 \text{ cm}^{-1}$) and the absence of ligand peaks in the FTIR of the precipitate. The TLC of the solute indicated the presence of the ligand. Also, addition of aqueous ammonia to the blue powder and extraction of the resulting solution with dichloromethane indicated no ligand as verified by TLC. This clearly indicates that the copper complexes of HL^{Me3} and HL^{Ph3} are not stable in basic conditions unless the reaction is carried out in methanol.

These results imply that the structural differences of the ligands impact the formation of their copper complexes. Apparently, the anionic amidate form of this ligand family is stabilized only when the steric effect of the R group is minimal. Therefore, HL and HL^{Ph} with lower steric bulk both get deprotonated and stabilize the anionic form of the ligand whereas HL^{Me3} and HL^{Ph3} do not.

Aside from crystallographic characterization of the complexes (vide infra), they were characterized by elemental analysis, UV/Vis

spectroscopy, FTIR, EPR and mass spectrometric techniques. The electronic spectrum of complex 1 in acetonitrile exhibits a d–d transition at 649 nm. Complexes 2 and 3 in methanol show similar electronic spectral patterns exhibiting d–d transitions at 689 and 704 nm, respectively, indicative of similar core structures with distorted square-pyramidal geometry. The IR spectrum of 1 has characteristic v_{OH} stretches for the waters and hydroxides centered at 3432 cm⁻¹, while 2 and 3 exhibit v_{OH} stretches characteristic of methanol at 3440 cm⁻¹. The N–H stretch of the amide group in the ligands of 2 and 3 occurs at 3347 cm⁻¹. The perchlorate stretch for 1 is observed at 1100 cm⁻¹. Finally, a sharp peak in the spectra of 2 and 3 is observed at 2807 cm⁻¹ and is assigned to the OMe⁻ anion.

To probe the solution state magnetic properties of these systems, ¹H NMR, EPR and magnetic measurements using the Evans method were carried out. Complex 1 is structurally similar to the previously reported cluster complex, $[Cu_8L_8(OH)_4](ClO_4)_4$.⁴ In particular, 1 has four copper ions bridged via two hydroxide ligands to form a tetracopper cluster (vide infra), and this tetracopper cluster is isostructural with half of the $[Cu_8L_8(OH)_4]^{4+}$ cation. Solutions of $[Cu_8L_8(OH)_4](ClO_4)_4$, which were shown to contain the full [Cu₈L₈(OH)₄]⁴⁺ fragment by electrospray mass spectrometry and conductance, are EPR silent. Magnetic susceptibility measurements for $[Cu_8L_8(OH)_4](ClO_4)_4$ showed that partially frustrated interactions among the four Cu ions making up each half of the cluster gave good agreement with the data, with $J_c =$ 106 cm⁻¹ and integer-spin ground and excited states, explaining the absence of the EPR signal despite being paramagnetic.⁴ Complex 1, as expected, exhibits several paramagnetically shifted signals in the region from 0-145 ppm. The exchange coupling of unpaired spins of the copper(II) ions shortens the electronic relaxation time from 10^{-9} s.⁸ This results in relatively sharp signals due to ligand protons spanning a broader spectral window. Signals that are shifted far downfield may be due to pyridyl protons, signals between 25-50 ppm could be due to methylene protons and signals between 5-20 ppm may be attributed to phenyl ring protons. The ¹H NMR spectrum of [Cu₈L₈(OH)₄](ClO₄)₄ is also distinguished by relatively sharp signals spread over a broad spectral window.⁴ The observed magnetic moment of 1.64 μ_B per Cu for 1 and its EPR silence are consistent with the magnetic properties of its structurally related analogue, $[Cu_8L_8(OH)_4](ClO_4)_4$.

Complexes 2 and 3 exhibit broadened ¹H NMR spectra with signals in a narrow spectral window of 0–10 ppm. Being dinuclear, complexes 2 and 3 are expected to have signals spanning a broader spectral window. However both 2 and 3 have broad and featureless NMR signals, suggesting the formation of mononuclear species in solution. Complexes 2 and 3 in CH₃CN and MeOH show axial EPR spectra which are nearly identical and may be attributed to mononuclear species in solution. Integration of the EPR signals for 2 and 3 reveals that in fact only a fraction of the species in solution are paramagnetic. Assuming a dimer-monomer equilibrium, just 3.2% of 2 and 5.8% of 3 dissociate into monomer, according to the quantitation of the EPR signals by integration. The g values clearly indicate typical tetragonal copper geometry of the paramagnetic species in 2 and 3. The observed magnetic moments in solution from Evans measurement of 2 and 3 are 1.19 and 1.17 μ_B per Cu, respectively. These values are consistent with an antiferromagnetically coupled dimer with a small fraction of paramagnetic monomer in solution.

The electrospray ionization mass spectra (ESI-MS) of **2** and **3** are in agreement with their dinuclear composition. For complex **2**, a peak at 721.1 m/z is assigned to the ion $[Cu_2(HL^{Me3})_2-(OMe)_2(OTf)]^+$ where the coordinated methanol molecules and one triflate anion are missing from **2**. Complex **3** has a peak at 1095.2 m/z that is assigned to the ion $[Cu_2(HL^{Me3})_2(OMe)_2(OTf)]^+$ that likewise has lost the coordinated methanol molecules and one triflate anion.

X-Ray crystal structures

Structure of 1. The molecular structure of 1 contains two slightly different independent tetranuclear motifs of $[Cu_4(L^{Ph})_4(OH)_2]^{2+}$, henceforth referred to as cluster A and cluster B. A line drawing of the structure is presented in Scheme 2, thermal ellipsoid representations are shown in Fig. 1, and selected bond lengths and angles are listed in Table 1. Each tetranuclear assembly is composed of four L^{Ph-} ligands, two µ₃-hydroxo ligands and four copper ions. The μ_3 -hydroxo ligands bridge two copper centers (Cu1A and Cu2A in cluster A; Cu1B and Cu1B' in cluster B), forming dimeric Cu_2O_2 units. The μ_3 -hydroxo ligands also coordinate to two other copper ions in each cluster (Cu3A and Cu4A in cluster A; Cu 2B and Cu2B' in cluster B). The Cu₂O₂ units deviate from planarity by 12.2 and 13.0° for clusters A and B, respectively. The Cu-O-Cu angles range from 96.3-130.0° and the Cu–O distances are in the range of 1.938–2.039 Å. These relatively large angles contribute to the Cu ··· Cu distances ranging from 2.98–3.58 Å. Many examples of hydroxide bridged copper complexes have been reported, particularly with respect to the relationship between the degree and type of magnetic exchange.9

In cluster A, in addition to the two μ_3 -OH bridging groups, Cu1A and Cu2A are coordinated by the chelating pair of N atoms from the pyridyl and amidate groups of two ligands and a carbonyl O atom from a separate ligand, making each metal center fivecoordinate. The metal centers Cu1A and Cu2A are about 0.19 and

Table 1 Selected bond parameters (Å, °) for 1

Cluster A				
Cu1A–Cu2A	2.9838(7)	Cu1A–N1A	1.9884(19)	
Cu1A-Cu3A	3.0792(6)	Cu1A–N8A	1.9282(19)	
Cu2A–Cu3A	3.5820(6)	Cu2A–N1B	1.986(2)	
Cu4A-Cu1A	3.4658(6)	Cu2A–N8B	1.937(2)	
Cu4A–Cu2A	3.0587(6)	Cu3A–N1C	2.010(2)	
Cu1A–O2A	1.9384(16)	Cu3A–N8C	1.967(2)	
Cu2A–O2A	2.0375(16)	Cu4A–N1D	1.989(2)	
Cu2A–O1A	1.9664(16)	Cu4A–N8D 1.970(2		
Cu3A–O1A	1.9861(16)	Cu1A-O1A-Cu3A	99.80(7)	
Cu4A–O2A	1.9850(16)	Cu2A–O1A–Cu3A	129.98(8)	
Cu1A-O1A-Cu2A	96.29(7)	Cu4A-O2A-Cu1A	124.10(8)	
Cu1A–O2A–Cu2A	97.23(7)	Cu4A–O2A–Cu2A 98.99(7)		
Cluster B				
Cu1B-Cu2B	3.0413(6)	Cu1B–N1E	1.992(2)	
Cu1B–Cu1B'	2.9856(8)	Cu1B-N8E	1.942(2)	
Cu2B–O1B	1.9841(19)	Cu2B–N1F	1.999(3)	
Cu1B-O1B-Cu2B	98.28(8)	Cu2B–N8F	1.994(2)	
Cu2B–O1B–Cu1B'	126.42(9)	Cu1B-O1B	2.0369(18)	
Cu1B–O1B–Cu1B′	96.67(8)	Cu1B-O1B'	1.9589(18)	



Fig. 1 Thermal ellipsoid representation of the X-ray crystal structure of 1 (cluster A, top; cluster B, bottom). Thermal ellipsoids are drawn at the 30% level. The phenyl rings of the benzyl groups, perchlorate anions, solvent molecules, and all hydrogen atoms are omitted for clarity.

0.27 Å out of the least squares basal plane towards the carbonyl oxygen atoms O10D and O10C, respectively. Cu1A and Cu2A are distorted square pyramidal as evidenced from the value of the geometric parameter τ ,¹⁰ which is 0.09 and 0.32, respectively. Since the ligand chelates to one metal through the pyridyl and amidate N atoms, it becomes impossible for the carbonyl O atom to bind to the same metal. Cu3A is four-coordinate and Cu4A is five-coordinate. Both Cu3A and Cu4A are coordinated by the chelating pair of N atoms from the pyridyl and amidate groups of two ligands, a carbonyl O atom from a separate ligand and a μ_3 -OH group. Furthermore, the carbonyl oxygen O10C, which is coordinated to Cu2A, is also coordinated to Cu4A at a slightly longer Cu-O distance of 2.2781(16) Å. Cu4A is distorted square pyramidal ($\tau = 0.04$) and is 0.24 Å out of the least squares basal plane towards the carbonyl oxygen O10C. Within this unit there are hydrogen bonding interactions between the hydroxides and perchlorate oxygens.

The copper ions in cluster B are in a slightly different coordination environment than in cluster A. The center of symmetry in cluster B causes the carbonyl O atoms to coordinate differently, but the pyridyl and amidate N atoms, along with the hydroxo bridges, coordinate almost identically in clusters A and B. In cluster B, all four copper centers are five-coordinate. Cu1B and Cu1B' are distorted square pyramidal ($\tau = 0.15$) and are 0.19 Å out of the least squares plane towards the carbonyl oxygens O10F and O10F'. Cu2B and Cu2B' are also distorted square pyramidal ($\tau = 0.15$), and are 0.13 Å out of the least squares plane towards the carbonyl oxygens. Within this unit, too, there are hydrogen bonding interactions between the hydroxides and perchlorate oxygens.

The structure of 1 is considerably different from our earlier report of an octanuclear complex [Cu₈(L)₈(OH)₄](ClO₄)₄.⁴ $[Cu_8(L)_8(OH)_4](ClO_4)_4$ is made up of two tetranuclear fragments which are connected to each other via the carbonyl oxygen of the HL ligand. Additional structural stability is also provided by the hydrogen bonding interactions between the carbonyl oxygen atom and the hydroxide hydrogen atom. These interactions that hold the pieces of the cluster together are absent in 1, so the features that are unique to complex 1 are the presence of two independent, slightly dissimilar tetranuclear units that do not interact with each other. The closest interaction between cluster A and B in 1 is 3.55 Å, which is the distance between C5B and C5E'. The different structural arrangement of the cluster in 1 is likely due to the greater steric bulk of HL^{Ph} compared with HL in $[Cu_8(L)_8(OH)_4](ClO_4)_4$. There are, however, striking similarities between $[Cu_8(L)_8(OH)_4](ClO_4)_4$ and 1 with respect to the way the ligand chelates and the way the μ_3 -hydroxo binds.

Structures of 2 and 3. The crystal structures of 2 and 3 are illustrated in Fig. 2. Bond distances and angles relevant to the copper coordination sphere of both compounds are listed in Table 2. The copper complexes are isostructural with slight variation in bond lengths and angles. The structures of 2 and 3 consist of two Cu(II) ions with each metal bridged by two μ_2 -methoxide ligands. Terminal ligation is provided by the N(pyridyl) and O donors of HL^{Me3} and HL^{Ph3} for 2 and 3, respectively. A MeOH on each metal ion completes the coordination sphere in 2 and 3. As noted before, the amide N atoms of the ligands in 2 and 3 are protonated and hence do not coordinate to Cu, making HL^{Me3} and HL^{Ph3} bidentate N, O donor ligands.

The Cu(II) centers exhibit distorted square pyramidal coordination geometries with the solvent MeOH occupying the axial positions [Cu–O(axial) \sim 2.25 Å]. A pyridyl nitrogen, a carbonyl

Table 2Selected bond parameters (Å, $^{\circ}$) for 2 and 3

	2	3
Cu1Cu1A	2.9916(10)	2.9604(3)
Cu1–O2	1.927(3)	1.9213(8)
Cu1–O2A	1.919(3)	1.9283(8)
Cu1–N1	1.992(3)	1.9978(9)
Cu1–O1	2.006(3)	1.9982(8)
Cu1–O3	2.279(3)	2.2395(9)
Cu1-O2-Cu1A	102.15(14)	100.53(4)
O2-Cu1-O2A	77.85(14)	79.47(4)
O2-Cu1-N1	97.25(13)	96.49(4)
O2A-Cu1-N1	173.09(14)	175.08(4)
O2-Cu1-O1	169.45(13)	161.66(3)
O2A-Cu1-O1	93.48(12)	91.00(3)
N1-Cu1-O1	90.85(13)	92.11(4)
O2-Cu1-O3	97.18(12)	101.37(4)
O2A-Cu1-O3	93.94(12)	94.12(3)
N1-Cu1-O3	91.50(13)	89.42(4)
O1–Cu1–O3	89.33(12)	94.86(3)



Fig. 2 Representation of the X-ray crystal structures of 2 (top) and 3 (bottom) as 30% thermal ellipsoids. All hydrogen atoms except for the amide and methanol hydrogen atoms have been removed for clarity.

oxygen and two methoxo oxygens form the basal plane. Cu1 and Cu2 lie 0.09 Å out of the least squares basal plane in **2** and 0.16 Å in **3**, illustrating that the copper centers adopt distorted square pyramidal geometry. Estimates of the degree of distortion from ideal square pyramidal geometry obtained by applying τ^{10} further indicate geometries close to square pyramidal ($\tau = 0.06$ for Cu1 and Cu2 in **2** and 0.23 for the copper centers in **3**).

For both compounds, the Cu₂O₂ unit is planar as indicated by the Cu₋O–Cu₋O dihedral angle of 0°. The Cu ··· Cu distance in **2** and **3** is 2.99 and 2.96 Å, respectively. Similar trends are also observed in hydroxo and alkoxo bridged complexes,¹¹ like [Cu₂(Me₃tacn)₂(μ_2 –OH)₂](ClO₄)₂,¹² with planar Cu₂O₂ units where the Cu ··· Cu separation is 2.971(1) Å. However this behavior is in contrast to certain hydroxo and alkoxo bridged complexes where the Cu₂O₂ units adopt bent shaped conformations with shorter Cu ··· Cu separations.¹³ The Cu–O–Cu angles are 102.5 and 100.3° for **2** and **3**, respectively, and lie in the expected range for dinuclear copper complexes reported in the literature.^{11,14} The Cu–O_{methoxide} distances are similar to those reported in the literature.

Experimental

General

All reagents were purchased from commercial sources and used without further purification. Benzotriazole-1-yl-oxytripyrrolidinophosphoniumhexafluorophosphate (Py-BOP) was obtained from Novabiochem and used without further purification. Solvents were dried and purified under nitrogen using standard methods and distilled immediately before use. Melting points were determined with a Mel-Temp laboratory melting point apparatus (USA). ¹H NMR spectra were measured on a Varian 300 MHz spectrometer using solvent as an internal standard $[{}^{1}\text{H} \delta \text{ (CHCl}_{3}) = 7.27 \text{ ppm}; {}^{1}\text{H} \delta \text{ (CH}_{3}\text{CN}) = 1.94 \text{ ppm}; {}^{13}\text{C} \delta$ $(CHCl_3) = 77.23$ ppm]. Elemental analyses were carried out by Atlantic Microlabs (Norcross, GA). Mass spectra were recorded on a Q-TOF quadrupole time-of-flight mass spectrometer (Micromass, Manchester, U.K.) equipped with a Z-spray electrospray ionization (ESI) source. Electronic spectra were measured on a Shimadzu UV2401PC UV-Vis spectrophotometer. IR spectra were recorded on a Nexus 470 FTIR spectrometer. X-Band EPR spectra were recorded on a Bruker EMX spectrometer at 100 K as frozen solutions. Quantitation of signals was performed using the method of Aasa and Vänngård¹⁵ with a copper sulfate solution (1.64 mM CuSO₄, 20% glycerol, 2.0 M NaClO₄, 0.1 M HCl) as an integration standard. Solution magnetic moment measurements were measured using the Evans method.¹⁶

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Although no problems were encountered in this work, only small amounts of material should be prepared and handled with caution.

2-Phenyl-N-(2-pyridylmethyl)acetamide (HL^{Ph}). The synthesis of HL^{Ph} was carried out via a modified procedure based on a published method.¹⁷ A solution of phenylacetyl chloride (1.55 g, 10 mmol) in anhydrous dichloromethane (10 mL) was added to a solution of 2-aminomethyl pyridine (1.08 g, 10 mmol) and triethylamine (1.32 g, 13 mmol) in anhydrous dichloromethane (15 mL) at 0 °C dropwise over 15 min. The solution became pale vellow and developed a precipitate. The solution was warmed to room temperature and after stirring for 24 h, the solvent was removed under vacuum. The resulting solid was dissolved in dichloromethane and washed with saturated sodium bicarbonate solution followed by water. The resulting solution was dried with anhydrous magnesium sulfate and the solvent was removed under vacuum. The remaining solid was crystallized from toluene to give HL^{Ph} as pale colorless crystals. Yield: 2.20 g (95%). Mp = 105-106 °C. Anal. Calcd for C₁₄H₁₄N₂O: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.13; H, 6.31; N, 12.35. ¹H NMR (300 MHz, CHCl₃d): δ 3.60 (d, 2H), 4.48–4.50 (d, 2H), 6.76 (s, 1 H), 7.13–7.33 (m, 7H), 7.59–7.65 (m, 1H), 8.41–8.43 (d, 1H) ppm. FTIR (KBr): 3277, 3078, 3032, 2922, 2362, 2337, 1642, 1601, 1588, 1557, 1493, 1471, 1455, 1435, 1420, 1344, 1318, 1267, 1199, 1168, 1155, 1098, $1048, 1030, 994, 749, 702, 693, 642, 624, 605, 531, 491, 405 \text{ cm}^{-1}$.

2,2-Dimethyl-N-(2-pyridylmethyl)propionamide (HL^{Me3}). The synthesis of HL^{Me3} was carried out via a modified procedure based on a published method.18 A solution of trimethylacetyl chloride (3.69 g, 30 mmol) in anhydrous THF (10 mL) was added to a solution of 2-aminomethyl pyridine (3.24 g, 30 mmol) and triethylamine (3.95 g, 39 mmol) in anhydrous THF (15 mL) at 0 °C dropwise over 15 min. The reaction was warmed to room temperature and after stirring for 24 h the solvent was removed under vacuum. The resulting oil was dissolved in dichloromethane and washed with saturated sodium bicarbonate solution followed by water. The resulting yellow solution was dried with anhydrous magnesium sulfate and the solvent was removed under vacuum to give HLMe3 as a yellow oil. Yield: 4.74 g (82%). Anal. Calcd for C₁₁H₁₆N₂O·1/4H₂O: C, 67.15; H, 8.45; N, 14.24. Found: C, 67.20; H, 8.56; N, 14.43. ¹H NMR (300 MHz, CHCl₃-d): δ 1.24–1.27 (m, 9H), 4.52-4.54 (d, 2H), 7.05 (s, 1H), 7.17-7.27 (m, 2H), 7.63-7.68 (t, 1H), 8.55 (d, 1H) ppm. FTIR (neat): 3297, 3063, 2952, 1511, 1366, 1299, 1202, 1149, 1099, 1070, 1049, 1012, 936, 889, 862, 751, 610, 528 cm⁻¹.

2,2,2-Triphenyl-N-(2-pyridylmethyl)acetamide (HL^{Ph3}). A solution of triethylamine (1.59 g, 15.6 mmol) in anhydrous DMF (5 mL) was added to a suspension of triphenyl acetic acid (1.5 g, 5.2 mmol) and 2-aminomethyl pyridine (0.563 g, 5.2 mmol) in anhydrous DMF (10 mL) dropwise over 5 min. The resulting suspension was cooled to 0 °C and Py-BOP (2.7 g, 5.2 mmol) in anhydrous DMF (5 mL) was added dropwise. The solution became yellow and completely clear. After stirring overnight, the resulting solution was poured into water (60 mL) with stirring. The resultant precipitate was collected, washed with water (2 \times 10 mL) and dried under vacuum to give HL^{Ph3} as a white solid. Yield: 1.86 g (94%). Colorless crystals were obtained by dissolving the powder in a mixture of toluene and dichloromethane. Mp =161–163 °C. Anal. Calcd for $C_{26}H_{22}N_2O$: C, 82.51; H, 5.86; N, 7.40. Found: C, 82.67; H, 5.84; N, 7.45. ¹H NMR (300 MHz, CHCl₃-*d*): δ 4.62–4.63 (d, 2H), 7.03 (bs, 1H), 7.10–7.14 (t, 1 H), 7.17–7.29 (m, 16 H), 7.56–7.62 (t, 1H), 8.39 (d, 1H) ppm. ¹³C{¹H} NMR (75 MHz, CHCl₃-d): δ 45.51, 67.98, 122.29, 122.42, 127.13, 128.1, 130.8, 143.57, 149.13, 156.66, 173.62 ppm. FTIR (KBr): 1603, 1525, 1491, 1441, 1352, 1323, 1269, 1254, 1236, 1102, 970, 928, 902, 792, 765, 738, 698, 673, 641, 621, 577, 533, 519, 461, 432 cm^{-1} .

[Cu₄(L^{Ph})₄(OH)₂](ClO₄)₂ (1). A methanolic solution of HL^{Ph} (0.150 g, 0.663 mmol) and triethylamine (0.147 ml, 1 mmol) was added to a methanolic solution of Cu(ClO₄)₂·6H₂O (0.245 g, 0.663 mmol) with constant stirring. The blue precipitate was collected by filtration, washed with methanol and dried under vacuum. Yield: 0.2058 g (89%). Anal. Calcd for C₅₆H₅₄Cl₂Cu₄N₈O₁₄: C, 48.45; H, 3.92; N, 8.07. Found: C, 47.96; H, 3.89; N, 8.04. UV-Vis [CH₃CN, λ_{max} , nm (ε , M⁻¹ cm⁻¹)]: 330 (sh, 5200), 649 (750). ¹H NMR (CH₃CN-d₃, 300 MHz, RT): δ 1.13, 3.43, 4.59, 5.67, 5.82, 7.29, 7.44, 7.9, 8.39, 9.33, 11.70, 13.23, 14.56, 24.37, 26.81, 36.08, 40.86, 43.51, 44.06, 93.08, 93.50, 122.19, 144.54 ppm. FTIR (KBr): 3432 (ν_{OH}), 1610, 1576, 1487, 1427, 1406, 1352, 1284, 1220, 1095 (ν_{ClO4}^{-}), 1028, 927, 846, 764, 722, 709, 656, 624, 563 cm⁻¹. Magnetic moment (Evans, CH₃CN-d₃): 1.64 μ_B/Cu(II).

 $[Cu_2(HL^{Me3})_2(OMe)_2(MeOH)_2](OTf)_2$ (2). A solution of HLMe3 (0.144 g, 0.75 mmol) and triethylamine (0.104 ml, 0.75 mmol) in dichloromethane was added to a methanolic solution of Cu(OTf)₂ (0.271 g, 0.75 mmol), forming a clear dark green solution. Vapor diffusion of diethyl ether resulted in the formation of green crystals of the product, 2. Yield: 0.320 g (91%). Anal. Calcd for C₂₈H₄₆Cu₂F₆N₄O₁₂S₂·1.5H₂O: C, 34.92; H, 5.13; N, 5.82. Found: C, 34.09; H, 4.18; N, 6.58. ESI-MS (CH₃OH): m/z = 721.1, $[Cu_2(HL^{Me3})_2(OMe)_2OTf]^+$; 691.1, [Cu₂(HL^{Me3})₂(MeOH)(OTf)]⁺; 404.0, [Cu(HL^{Me3})(OTf)]⁺; 255.1, $[Cu(HL^{Mc3})]^+$. UV-Vis [CH₃OH, λ_{max} , nm (ϵ , M⁻¹, cm⁻¹)]: 292 (4300), 350 (sh, 1700), 704 (124). FTIR (KBr): 3400 (v_{OH}), 3347 (v_{NH}), 2807 (v_{OMe}), 1970, 1821, 1611, 1511, 1447, 1366, 1252, 1166, 1032, 906, 844, 774, 701, 672, 638, 641, 528, 464 cm⁻¹. EPR (9.44 MHz, mod. freq. 100 kHz, mod. amp. 6 G, MeOH, 100 K): $g_{\parallel} = 2.284, g_{\perp} = 2.05, A_{\parallel} = 140$ G. Magnetic moment (Evans, CH₃OH-*d*₄): 1.19 μ_B/Cu(II).

[Cu₂(HL^{Ph3})₂(OMe)₂(MeOH)₂](OTf)₂ (3). A solution of HL^{Ph3} (0.055 g, 0.15 mmol) and triethylamine (0.014 ml, 0.15 mmol) in dichloromethane was added to a methanolic solution of Cu(OTf)₂ (0.053 g, 0.15 mmol) forming a clear dark green solution. Vapor diffusion of diethyl ether resulted in the formation of green crystals of the product, **3**. Yield: 0.100 g (95%). Anal. Calcd for C₅₈H₅₈Cu₂F₆N₄O₁₂S₂: C, 53.25; H, 4.47; N, 4.28. Found: C, 52.34; H, 4.22; N, 4.45. ESI-MS (CH₃OH): *m/z* = 1095.2, [M–OTf–2MeOH]⁺; 472.2, [Cu(HL^{Ph3})(MeOH)]⁺; 441.1, [Cu(HL^{Ph3})]⁺. UV-Vis [CH₃OH, λ_{max}, nm (ε, M⁻¹, cm⁻¹)]: 290 (3300), 689 (159). FTIR (KBr): 3400 (ν_{OH}), 3349 (ν_{NH}), 2807 (ν_{OMe}), 1970, 1821, 1611, 1528, 1447, 1384, 1252, 1166, 1032, 906, 844, 774, 701, 672, 638, 641, 517, 464 cm⁻¹. EPR (9.44 MHz, mod. freq. 100 kHz, mod. amp. 8 G, MeOH, 100 K): $g_{\parallel} = 2.284$, $g_{\perp} = 2.05$, $A_{\parallel} = 140$ G. Magnetic moment (Evans, CH₃OH- d_4): 1.17 μ_B/Cu(II).

X-Ray crystal structure determination

Single crystals of 1-3 were obtained by either slow evaporation of methanol or acetonitrile solutions of the complex or by vapor diffusion of diethyl ether into solutions of the complex. Intensity data for 1-3 were collected using an instrument with a Bruker APEX ccd area detector¹⁹ with graphite-monochromated Mo Ka ($\lambda = 0.71073$ Å) radiation. Cell parameters were determined from a non-linear least squares fit of the data. The data were corrected for absorption by the semi-empirical method.²⁰ The structures were solved by direct methods and refined by full-matrix least squares methods on F^{2.21} Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data for 1-3 are summarized in Table 3. In complex 1, the four perchlorate anions and solvent molecules (acetonitrile and water) were severely disordered. The solvent molecules were best modeled using the Squeeze program.²² The atoms C(12E)-C(17E) were disordered and modeled in two orientations. The occupancies of these atoms refined to 0.532(6) and 0.468(6) for the unprimed and primed atoms. The occupancies of the disordered anion Cl(1I)-O(4I) refined to 0.499(5) and 0.501(5) for the unprimed and primed atoms. Restraints on the positional and displacement parameters of the disordered atoms were required.

CCDC reference numbers 285146, 285147 and 285410.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513763b

Conclusions

The synthesis and structural characterization of a family of copper complexes were carried out using a variety of sterically hindered pyridylamide ligands synthesized in our laboratory. The copper complexes that form are sensitive to the steric properties of the pyridylamide ligand used. We demonstrate the possibility to obtain selectively mono-, bi-, tetra- and octanuclear complexes by tuning synthetic parameters (steric effects of ligand, solvent, and stoichiometry of the base). In the complete absence of a base, mononuclear complexes form with all of the pyridylamide ligands.^{4,7} However, when triethylamine is added to deprotonate the amide N, the presence of triphenyl and trimethyl substituents

Table 3	Crystallographic data for 1-3	3
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	$1.2CH_3CN.3H_2O$	2 ·1.5H ₂ O	3	_
Formula	$C_{60}H_{66}Cl_2Cu_4N_{10}O_{17}$	$[C_{56}H_{98}Cu_4F_{12}N_8O_{27}S_4]_{1/2}$	$C_{58}H_{58}Cu_2F_6N_4O_{12}S_2$	
M	1524.29	962.91	1308.32	
Temperature/K	95(2)	203(2)	110(2)	
Space group	C2/c	<i>P</i> -1	P-1	
a/Å	42.218(8)	9.080(2)	11.3265(8)	
b/Å	17.377(3)	10.766(3)	12.2802(8)	
c/Å	26.792(5)	11.438(3)	12.5623(9)	
a/°	90	76.204(3)	83.3530(10)	
β/°	103.224(5)	80.283(3)	63.4270(10)	
y/°	90	77.456(3)	70.6400(10)	
Ż	12	1	1	
$V/Å^3$	19134(6)	1051.8(4)	1473.27(18)	
$\rho_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.587	1.520	1.475	
μ/mm^{-1}	1.477	1.198	0.876	
$R1 \left[I > 2\sigma(I) \right]$	0.0351	0.0704	0.0264	
$wR2[I > 2\sigma(I)]$	0.1050	0.1781	0.0747	
GOF on F^2	1.013	1.099	1.042	

on the pyridylmethyl ligand (HLPh3 and HLMe3) results in clean isolation of binuclear complexes 2 and 3. We hypothesize that the steric constraints of HL^{Ph3} and HL^{Me3} lead to the preferential formation of the methoxide bridged species rather than clusters. The ligand binding mode in 2 and 3 is bidentate via the pyridyl N and amide O donor atoms. This same binding mode was observed with HL when a mononuclear complex formed in the absence of base.⁴ However, HL^{Ph}, which contains a benzyl substituent with reduced steric bulk, exclusively forms a hydroxo bridged tetranuclear complex, 1. The binding mode of the ligand in 1 is similar to the octanuclear copper cluster with HL, where the amide nitrogen has been deprotonated to form the amidate ligand.⁴ In the octanuclear cluster and 1, the anionic amidate N atom coordinates to copper, providing the means by which clusters can form. The less sterically hindered HL and HL^{Ph} are able to form clusters, while HL^{Me3} and HL^{Ph3}, which are much more sterically encumbered, cannot.

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