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Syntheses and structures of a phenoxo-bridged copper(II) distorted cubane and related complexes with 2-hydroxy-*N*-(2-pyridylalkyl)benzamide ligands

Zhaodong Wang, Douglas R. Powell, Robert P. Houser*

Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019, USA

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ABSTRACT

Two new pyridylakylamide ligands containing phenol groups appended to the amide, 2-hydroxy-*N*-(2-pyridylmethyl)benzamide (HL^{PhOH}) and 2-hydroxy-*N*-(2-pyridylethyl)benzamide (HL^{PhOH'}), were synthesized. Copper(II) complexes of these ligands were synthesized and characterized by X-ray crystallography, ESI-MS, FTIR, UV/Vis, and EPR spectroscopy. When basic Et₃N was used to deprotonate the ligands, tetra-copper(II) [Cu₄(L^{PhO})₄] (1) or dicopper(II) [Cu₂(L^{PhO'})₂(CH₃OH)₂] (3) were formed. When base was not used, mononuclear [Cu(HL^{PhOH})₂Cl₂] (2) resulted. Complex 1 possesses a distorted cubane-like structure, with the ligands bridging via the phenoxo oxygen atoms, and the copper atoms possessing a distorted square planar geometry. The ligands in dimeric complex 3 also bridge between copper(II) atoms via the phenoxo oxygen atoms, and the copper atoms are square pyramidal. Monomeric 2 is a tetragonally distorted six-coordinate species with pyridyl N atoms and chloride ligands in the equatorial plane, and long interactions with the amide carbonyl O atoms in the axial positions.

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Polynuclear copper clusters have attracted much attention due to their relevance in bioinorganic modeling chemistry, as well as interest in their magnetic properties. The Cu_4O_4 unit is the most widely investigated member of the larger class of M_4O_4 clusters. Hydroxo- or alkoxo-bridged tetranuclear copper complexes with cubane-like structures have been synthesized and characterized, with particular attention given to their magnetic properties [1,2]. In most cases, the copper is five-coordinate with N or O donors from different organic ligands, forming a square pyramidal geometry. There is only one reported hydroxo-bridged, four-coordinate copper complex with an open cubane-like Cu_4O_4 framework [3]. Here, we reported the first four-coordinate phenoxo-bridged tetranuclear copper complex with distorted cubane geometry.

Recently, our laboratory has focused on the synthesis and characterization of copper clusters using a series of pyridylmethylamide ligands [4–10]. Pyridyl amide ligands exhibit totally different coordination modes depending on the presence or absence of base used in the synthesis of complexes, since a base will deprotonate the amide group. In addition, different substituents connected to the amide result in different coordination geometries of the copper complexes due to steric considerations. An octanuclear copper(II) complex, $[Cu_8L_8(OH)_4](ClO_4)_2$, with bridging amidate L⁻ ligands, where HL = *N*-(2-pyridylmethyl)acetamide, was the first example of multicopper species synthesized in our laboratory [9]. More recently, other multicopper complexes with pyridylmethylamide ligands containing alkyl or aryl groups in place of the methyl group in HL (HL^{Ph}, HL^{Me3}, and HL^{Ph3}) were also reported, including hydroxo- and methoxo-bridged complexes $[Cu_4(L^{Ph})_4(OH)_2]$ (ClO₄)₂, $[Cu_2(HL^{Me3})_2(OMe)_2](OTf)_2$ and $[Cu_2(HL^{Ph3})_2(OMe)_2](OTf)_2$ [8]. Here we report two new ligands and their copper(II) complexes where we have introduced a phenol group into the pyridyl amide ligand as shown in Scheme 1.

Two new ligands were designed based on pyridylamide ligands previously synthesized in our laboratory [5–12], by replacing the alkyl or aryl functional group in HL^R with a phenol group (see Scheme 1). 2-Hydroxyphenyl-*N*-(2-pyridylmethyl)acetamide (HL^{PhOH}) and 2-hydroxyphenyl-*N*-(2-pyridylethyl)acetamide (HL^{PhOH'}) differ only in the number of carbon atoms connecting the pyridyl group to the amide group. Both ligands were synthesized by the coupling reaction between salicylic acid and the corresponding 2-aminoalkylpyridine in the presence of DCC and HOBT [13].

Addition of Cu(OTf)₂ dissolved in CH₃OH to a stirred CH₃OH solution of HL^{PhOH} and Et₃N led to the formation of a dark green solution from which dark green crystals of $[Cu_4(L^{PhO})_4]$ (1) were isolated [13,14]. Crystallographic analysis shows that **1** is a tetra-nuclear copper(II) cluster, with a distorted cubane structure (Fig. 1 and S1). The neutral $[Cu_4(L^{PhO})_4]$ complex consists of four copper(II) atoms and four fully deprotonated $(L^{PhO})^{2-}$ ligands. Each copper center is four-coordinate square planar with two N donors (pyridyl and amidate groups) and one phenoxo O donor from one ligand, and the fourth coordination site occupied by another phenoxo O donor from a second ligand. The nearly square planar geometry is supported by a τ_4 value of 0.04, where a value of 0.0

^{*} Corresponding author. Tel./fax: +1 405 325 3551. *E-mail address:* houser@ou.edu (R.P. Houser).

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Scheme 1. Ligands used in this study: HL^{PhOH} and $HL^{PhOH'}$. The amide NH and the phenol OH can be deprotonated to produce divalent anionic ligands $(L^{PhO})^{2-}$ and $(L^{PhO'})^{2-}$.

corresponds to perfect square planar and a value of 1.0 corresponds to perfect tetrahedral [5]. The Cu₄O₄ core structure forms a distorted cube, with four Cu and four O atoms occupying alternate vertices. The four copper atoms are bridged by four μ_2 -phenoxo atoms. The Cu-N and Cu-O bond lengths are typical for copper(II) complexes, and the trans angles of the square planar copper centers are in the range of 175.67–179.20°, which supports the slightly distorted square-planar geometry assignment. The phenoxo-bridged Cu---Cu distances are 3.279 Å for Cu1B---Cu1C and 3.291 Å for Cu1A...Cu1B, while the unbridged Cu...Cu distances are 3.218 Å for Cu1B···Cu1D and 3.288 Å for Cu1A···Cu1C. Additional weak interactions in the apical positions of the copper coordination sphere are evident from the long $Cu \cdots O(phenoxo)$ distances. There is little difference between these distances, with the Cu···O(phenoxo) distances in the apical positions of 3.727 Å (Cu1A···O17D) and 3.690 Å (Cu1B···O17A). There are strong $\pi \cdots \pi$ interactions between the pyridyl and phenoxo aromatic rings, with centroid-centroid distances of 3.426 Å and 3.727 Å. The $\pi \cdots \pi$ interactions, which are an important class of noncovalent intermolecular forces [15], have an almost perfect face-to-face alignment in **1**.

The ESI-MS data for complex **1** in CH₃OH indicates the presence of the cluster complex in solution. The peak at m/z = 601.90 corresponds to a dication comprised of the cluster plus two sodium ions, $\{[Cu_4(L^{PhO})_4] + 2Na\}^{2+}$, while the peak at m/z = 1181.06 corresponds to the cluster plus one sodium ion, $\{[Cu_4(L^{PhO})_4] + Na\}^{+}$.



Fig. 1. Representation of the X-ray crystal structure of **1**. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu1A–N1A, 1.9948(16); Cu1B–N1B, 1.9910(16); Cu1A–N8A, 1.8892(16); Cu1B–N8B, 1.8961(16); Cu1A–O17A, 1.9451(13); Cu1A–O17B, 1.9906(13); Cu1B–O17B, 1.9619(14); Cu1B–O17C, 1.9833(13); N8A–Cu1A–O17A, 94.36(6); N8A–Cu1A–N1A, 84.60(7); N8A–Cu1A–O17B, 175.67(6); O17A–Cu1A–O17B, 85.42(5); O17B–Cu1A–N1A, 95.63(6); O17A–Cu1A–N1A, 178.95(6). See Figure S1 for the thermal ellipsoid plot of **1**.

Several factors determine the magnetic properties of the Cu₄O₄ clusters, including Cu–O distances, Cu–··Cu distances, Cu–O–Cu bond angles, and the geometry of copper and oxygen. The Cu–O–Cu bond angle is the major factor that controls the magnetic interactions. Magnetic measurements were carried out on solutions of **1** by the Evans method. The effective magnetic moment (μ_{eff}) value of 1.813 BM/Cu suggests no antiferromagnetic interactions between the copper atoms in **1**, in contrast to other complexes, perhaps due to the larger Cu–O–Cu bond angles (112.8–113.2°) in **1** [16,17]. The typical axial X-band EPR spectrum of complex **1** further supports the absence of magnetic interactions between copper(II) ions in the cluster.

Using CuCl₂ instead of Cu(OTf)₂, and without base present to deprotonate HL^{PhOH} , mononuclear complex $[Cu(HL^{PhOH})_2Cl_2]$ (2) was synthesized [13,18]. The absence of base in the synthesis of **2** results in the NH and OH groups not coordinating to the copper atom. We also tried the same reaction with CuCl₂ in the presence of Et₃N, but crystals suitable for X-ray analysis were not isolated. The structure of 2, as revealed by X-ray crystallographic analysis, consists of a mononuclear copper complex with one copper(II), two neutral HL^{PhOH} ligands, and two chloride ligands (Fig. 2). The copper is tetragonally distorted six-coordinate with two pyridyl N atoms from the ligands and two chlorides making up the equatorial plane, and long interactions with amide carbonyl O atoms in the axial positions. The Cu-N and Cu-Cl distances in 2 are typical for these bonds, and the longer Cu-O distance of 2.5557(14) Å in the apical positions indicate weak interactions between Cu and the amide carbonyl O atoms. There is intramolecular hydrogen bonding between the carbonyl O and OH from the phenol group, with a O1...O2 distance of 2.695 Å and a O1–H...O2 bond angle of 144°. Finally, there are intermolecular hydrogen bonding



Fig. 2. Representation of the X-ray crystal structure of **2** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Cu1–N1, 2.0408(15); Cu1–Cl1, 2.3062(6); Cu1–O2, 2.5557(14); N1–Cu1–Cl1, 91.33(4); N1–Cu1–Cl1, 88.75(4).

interactions between the Cl and the NH amide groups, with a $N \cdots Cl$ distance of 3.261 Å and a $N-H \cdots Cl$ bond angle of 156°.

Binuclear complex [Cu₂(L^{PhO'})₂(CH₃OH)] (**3**) was prepared by the same synthetic method as complex 1 using $Cu(OTf)_2$ and Et₃N in CH₃OH, but substituting the HL^{PhOH'} ligand for HL^{PhOH} [13,19]. In contrast to 1, the structure of 3 (Fig. 3) is significantly different, with a binuclear structure that consists of two copper ions and two deprotonated ligands (L^{PhO'})²⁻. The two copper atoms are bridged by two phenoxo O atoms, forming a Cu₂O₂ core structure. Each copper is five-coordinate with two N donors (pyridyl and amidate) and one phenoxo O donor from one ligand, and a phenoxo O donor from the second ligand making up the basal plane. The fifth coordination site is occupied by a methanol solvent molecule in the axial position, forming a distorted square pyramidal geometry, which is supported by a τ_5 value of 0.180 for **3**, where a value of 0.0 corresponds to perfect square pyramidal and a value of 1.0 corresponds to perfect trigonal bipyramidal [20]. The Cu-O_{MeOH} bond length of 2.3476(14) Å is longer than the Cu-O_{phenoxo} and Cu-N bond lengths in 3. The basal positions are occupied by two N atoms and two O atoms from the ligands. The N₂O₂ donor set is almost planar, and the Cu1 and Cu1A centers are displaced from the N_2O_2 mean plane by 0.1076 Å and 0.1215 Å, respectively, toward the coordinated methanol solvents. The $Cu \cdots Cu$ distance is 3.062 Å, which is similar to other reported phenoxo-bridged dicopper complexes [16,17,21-23].

The magnetostructural relationship in phenoxo-bridged binuclear copper complexes has been widely investigated. The effective magnetic moment (μ_{eff}) of complex **3** is 1.879 BM/Cu, which suggests no antiferromagnetic interaction between the two copper atoms. The X-band EPR spectrum of complex **3** is similar to complex **1**, and shows a typical axial signal, supporting the absence of magnetic coupling. The electrospray ionization mass spectra (ESI-MS) of **3** reveals the presence of the compound in solution, with a peak at m/z = 607.87 corresponding to $\{[Cu_2(L^{PhO'})_2] + H\}^+$ without the coordinated methanol molecules.



Fig. 3. Representation of the X-ray crystal structure of **3** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Cu1–N10, 1.9362(16); Cu1–N14, 1.9954(17); Cu1–O1, 1.9530(13); Cu1–O1', 1.9831(13); Cu1–O19, 2.3476(14); N10–Cu1–N14, 93.50(7); N10–Cu1–O19, 86.96(5); O1–Cu1–N14, 173.74(6); N14–Cu1–O19, 88.21(6); Cu1–O1-Cu1A, 102.13(6).

In summary, two new ligands, HL^{PhOH} and HL^{PhOH'}, were designed and synthesized as an extension to our previous work. Two multinuclear copper(II) complexes, **1** and **3**, were synthesized and characterized. In both complexes, the ligands have similar coordination modes, coordinating via the pyridyl N, amidate N, and phenoxo O atoms. The differences between HL^{PhOH} and $HL^{PhOH'}$ have some important steric effects on the nuclearity of the copper complexes. In tetranuclear 1, $(L^{PhO})^{2-}$ forms a five-membered ring between the copper and the pyridyl-amidate chelate, while in the binuclear **3**, $(L^{PhO'})^{2-}$ forms a six-membered ring between the copper and the pyridyl-amidate chelate, since $(L^{PhO'})^{2-}$ contains an additional carbon atom in the linkage between the pyridyl ring and the amide. In addition, the coordination mode of the copper is different, one is four-coordinate, and the other is five-coordinate. All of these differences illustrate the effects of ligand flexibility on the nuclearity and the coordination geometry in copper complexes with these ligands.

Acknowledgments

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Appendix A. Supplementary material

CCDC 725451, 725452, and 725453 contain the supplementary crystallographic data for **1**, **2**, and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Complete synthesis and characterization details for HL^{PhOH}, HL^{PhOH'}, and **1–3**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.04.007.

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- [13] See Supplementary Information for full synthetic and characterization details. [14] [Cu₄(L^{PhO})₄] (1). A solution of Cu(OTf)₂ (0.0905 g, 0.250 mmol) in methanol was added to a solution of HL^{PhOH} (0.114 g, 0.500 mmol) and triethylamine (0.147 ml, 1.00 mmol) in methanol, followed by vapor diffusion of diethyl ether into the solution (0.0456 g, 62.9% yield). Anal. Calcd. for C₅₂H₄₀Cu₄N₈O₈·2CH₃OH: C, 53.0; H, 4.0; N, 9.2. Found: C, 52.9; H, 4.4; N, 9.4. FTIR (KBr): 3750, 3435, 1772, 1733, 1695, 1653 (ν_C-0), 1599, 1587, 1548, 1444, 1383, 1215, 1162, 1097, 756, 619, 589, 516, 464 cm⁻¹. UV-vis (CH₃OH) [λ_{max}, nm (ε, mol⁻¹ cm⁻¹)]: 390 (1400), 611 (400). ESI-MS (CH₃OH) im/z = 601.98, {[Cu₄(L^{PhO})₄] + 2Na]²⁺; m/z = 1181.06, {[Cu₄(L^{PhO})₄] + Na]⁺. EPR (CH₃OH, 77 K, 9.455 GHz, 0.25 mW, mod. amp. 1 G): g_⊥ = 2.04, g_{||} = 2.246, A_{||} = 184 G. Magnetic moment (Evans method, 293 K, DMSO-d₆): 1.813 BM/Cu. Crystal data: Cs₄H₄₈Cu₄N₈O₁₀, *M*, = 1223.16 g mol⁻¹, monoclinic, space group C2/c, *a* = 24.617(5) Å, *b* = 17.336(4) Å, *c* = 13.445(3) Å, α = γ = 90°, β = 120.791(5)°, V = 4929.0(19) Å³, Z = 4, ρ_{calcd} = 1.648 g cm⁻³, λ(Mo_{6x}) = 0.71073 Å, *T* = 100(2) K, crystal dimensions 0.27 × 0.16 × 0.14 mm, μ(Mo_{6x}) = 0.71073 Å, *T* = 100(2) K, crystal difference map within 0.398 and −0.303 eÅ⁻³.
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- 35 (1996) 3117. [18] $[Cu(HL^{PhOH})_2Cl_2]$ (2). A solution of CuCl₂ (0.0340 g, 0.250 mmol) in methanol was added to a solution of HL^{PhOH} (0.117 g, 0.500 mmol) in methanol, followed by filtration and vapor diffusion of diethyl ether into the filtrate (0.094 g, 64% yield). Anal. Calcd. for C₂₆H₂₄Cl₂CuN₄O₄: C, 52.8; H, 4.1; N, 9.5. Found: C, 52.9; (1) Anar Catch for C26124C12C11404, C, 52.3, 11, 4.1, 11, 5.5, Found C, 52.3, 11, 4.1, 11, 15, 15, 1482, 1326, 1303, 1206, 957, 754, 677, 613, 545 cm⁻¹. UV-vis (CH₃OH) [λ_{max} , nm (ϵ , mol⁻¹ cm⁻¹)]: 400 (110). ESI-MS (CH₃OH): m/z = 578.93, [Cu₂(L^{PhO})(HL^{PhO})]^{*}; 290.07, [Cu(HL^{PhO})]^{*}; 229.13, [HL^{PhOH} + H]^{*}, EPR (CH₃OH, 77 K, 9.454 GHz, 0.63 290.07, $[Cu(RL^{-m})]$; 229.13, $[RL^{-m+1} + R]$, EPK $(CH_3OH, 7/K, 9.454 GH2, 0.63)$ mW, mod. amp. 1 G): $g_{\perp} = 2.045$, $g_{\parallel} = 2.228$, $A_{\parallel} = 169$ G. Magnetic moment (Evans method, 293 K, DMSO- d_6): 1.683 BM/Cu. Crystal data: $C_{26}H_{24}Cl_2CuN_4O_4$, $M_r = 590.93$ g mol⁻¹, monoclinic, space group $P2_1/c$, a = 11.662(2) Å, b = 8.0504(16) Å, c = 13.350(3) Å, $\alpha = \gamma = 90^{\circ}$, $\beta = 101.751(5)^{\circ}$, V = 1227.1(4) Å³, Z = 2, $\rho_{calcd} = 1.599$ g cm⁻³, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, T = 100(2) K, crystal dimensions $0.21 \times 0.19 \times 0.12$ mm, $\mu(Mo_{K\alpha}) = 1.150$ mm⁻¹, $\theta = 1.78$ -25.99°, 9242 measured reflections, 2407 independent reflections (R_{int} = 0.0274), R₁ = 0.0282, wR₂ = 0.0777, GOF = 1.005, 175 parameters, final
- difference map within 0.398 and -0.303 e^{-3} . [19] $[\text{Cu}_2(\text{L}^{\text{PhO'}})_2(\text{CH}_3\text{OH})_2]$ (3). A solution of Cu(OTf)₂ (0.0905 g, 0.25 mmol) in CH₃OH was added to a solution of HL^{PhOH'} (0.121 g, 0.50 mmol) and triethylamine (0.147 ml, 1.00 mmol) in methanol, followed by vapor

diffusion of diethyl ether into the filtrate (0.057 g, 68% yield). Anal. Calcd. for $C_{30}H_{32}Cu_2N_4O_6\colon$ C, 53.6; H, 4.8; N, 8.3. Found: C, 53.1; H, 4.6; N, 8.3. FTIR (KB7): 3446, 2946, 2842, 1608 ($v_{C=0}$), 1595, 1574, 1531, 1486, 1447, 1387, 1259, 1147, 1079, 887, 763, 703, 657, 586, 514, 427 cm⁻¹. UV-vis (CH₃OH) $[\lambda_{\text{max}}, \text{nm} (\varepsilon, \text{mol}^{-1} \text{ cm}^{-1})]: 620 (112). \text{ ESI-MS} (CH_3OH): m/z = 628.87,$ $[[Cu_2L_2^{PhO'}] + Na]^*; 607.87, [[Cu_2L_2^{PhO'}] + H]^*; 304.07, [Cu(HL^{PhO'})]^*. EPR (CH_3OH).$ $[CH_3OH]$ 77 K, 9.433 GHz, 1.89 mW, mod. amp. 20 G): $g_{\perp} = 2.05$, $g_{\parallel} = 2.257$, $A_{\parallel} = 176$ G. Magnetic moment (Evans method, 293 K, DMSO- d_6): 1.879 BM/Cu. Crystal data: C₃₀H₃₂Cu₂N₄O₆, M_r = 671.68 g mol⁻¹, triclinic, space group P1, a = 7.2285(12) Å, $\beta = 10.3814(16)$ Å, c = 11.0545(18) Å, $\alpha = 67.337(5)^{\circ}$, $\beta = 89.615(5)^{\circ}$, $\gamma = 70.128(5)^{\circ}$, V = 712.5(2) Å³, Z = 1, $\rho_{calcd} = 1.565$ g cm⁻³, $\lambda(Mo_{KZ}) = 0.71073$ Å, *T* = 100(2) K, crystal dimensions $0.39 \times 0.08 \times 0.08$ mm, $\mu(Mo_{K\alpha}) = 1.544$ mm⁻¹, θ = 2.02–26.00°, 5230 measured reflections, 2734 independent reflections $(R_{int} = 0.0141), R_1 = 0.0256, wR_2 = 0.0670, GOF = 1.018, 194$ parameters, final difference map within 0.368 and -0.235 eÅ-3.

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