

Copper(II) complexes of piperazine-derived tetradentate ligands and their chiral diazabicyclic analogues for catalytic phenol oxidative C–C coupling



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ABSTRACT

Reaction of the chiral ligands (1*S*,4*S*)-2,5-bis(6-methylpyridyl)-diazabicyclo[2.2.1]heptane (**L**¹) and (1*S*,4*S*)-2,5-bis(1-methyl-2-methylbenzimidazolyl)-diazabicyclo[2.2.1]heptane (**L**²) with CuCl₂ results in the hydroxo-bridged dicopper complexes [(**L**¹)Cu₂(μ-OH)(H₂O)Cl₃] (**3**), and [(**L**²)Cu₂(μ-OH)(H₂O)Cl₃] (**4**). Both chiral complexes were characterized spectroscopically, and **3** in the solid state by X-ray crystallography, confirming they are structurally related to their previously reported copper acetate analogues (**1** and **2**) due to their hydroxo-bridged bimetallic core. The achiral ligand analogues *N,N'*-bis(2-picolyl)piperazine (**L**³) and *N,N'*-bis(1-methyl-2-methylbenzimidazolyl)piperazine (**L**⁴) were employed to obtain the corresponding complexes with CuCl₂, affording the chloro-bridged [(**L**³)(CuCl)₂(μ-Cl)₂]_n (**5**) and [(**L**⁴)(CuCl)₂(μ-Cl)₂] (**6**), neither of which features a bridging hydroxo ligand; instead, complex **5** was structurally characterized as a coordination polymer. The acetate-derived complexes **1** and **2** are active in oxidative C–C coupling of 2,4-di-*tert*-butylphenol, while **3** and **4** have low activity; the achiral complexes **5** and **6**, lacking a bridging hydroxo ligand, are inactive in this reaction.

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Recent advances in the development of copper complexes that carry out selective oxidation reactions draw inspiration from the coordination environment in the active sites of various metalloenzymes. These include the dicopper tyrosinase [1], chatecol oxidase [2], and to a lesser extent methane monooxygenase [3]. Histidine as *N*-donor is ubiquitous in such non-heme metalloenzymes, which has led to the design and synthesis of nitrogen-rich ligands featuring pyridyl [4], pyrazolyl [5], imidazolyl [6], and bezimidazolyl groups [7]. Novel approaches for the development of catalysts inspired on the aforementioned enzymes have recently relied on the use of chelating ligands that provide a sufficiently preorganized coordination environment [8], which can be further tuned by the electronic properties of the donor groups to harness the synergistic reactivity of the bimetallic sites.

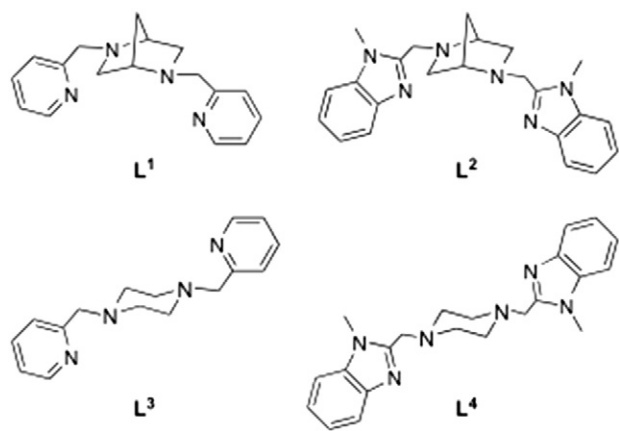
In this context, we recently reported the synthesis of novel binucleating ligands with pyridyl and benzimidazolyl groups appended to the nitrogen atoms of the enantiomerically pure (1*S*,4*S*)-2,5-diazabicyclo[2.2.1]heptane, resulting in the tetradentate ligands **L**¹ and **L**² (Scheme 1) [9]. Both compounds give rise to chiral hydroxo-bridged dicopper complexes irrespective of the amount of copper(II) acetate employed in the reactions, with Cu²⁺ ions at a distance of approximately 3.7 Å. We herein extend this work to the

analogous hydroxo-bridged dicopper complexes obtained from copper(II) chloride, as well as the achiral versions of the ligands bispicolyl- and bis(2-methylbenzimidazolyl)piperazine derivatives **L**³ and **L**⁴, differing only in the bridgehead methylene group of the diazabicyclo. The latter compounds were also employed for the preparation of the corresponding dicopper complexes with CuCl₂. The combined results of their competence as catalysts for oxidative phenol coupling reactions are presented.

Recently, we reported the synthesis and characterization of the products of the reactions between **L**¹ and **L**², and copper(II) acetate. In both cases dicopper complexes [(**L**²)Cu₂(μ-OH)(H₂O)(OAc)₂Cl] (**1**) and [(**L**¹)Cu₂(μ-OH)(H₂O)(MeOH)(OAc)₂OAc] (**2**) were obtained [9], even when only one equiv. of Cu²⁺ was employed in the reactions, indicating that these ligands favor the formation of hydroxo-bridged bimetallic species. This was extended to CuCl₂ as a source of Cu²⁺ ions to gauge the effect of the chloride counterions in the formation of the dinuclear complexes. Replacement of acetate for chloride resulted also in the formation of bimetallic complexes [(**L**¹)Cu₂(μ-OH)(H₂O)Cl₃] (**3**) and [(**L**²)Cu₂(μ-OH)(H₂O)Cl₃] (**4**), as determined in acetonitrile solution by ESI mass spectrometry: for **3**, a peak at *m/z* = 495 consistent with the cation [(**L**¹)Cu₂(μ-OH)Cl₂]⁺ was detected, while a similar species at *m/z* = 601 assigned to [(**L**²)Cu₂(μ-OH)Cl₂]⁺ was present in solutions of **4**; these bimetallic formulations are also consistent with combustion analysis [10]. Further characterization included IR spectroscopy, which

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Scheme 1. Ligands employed in this work.

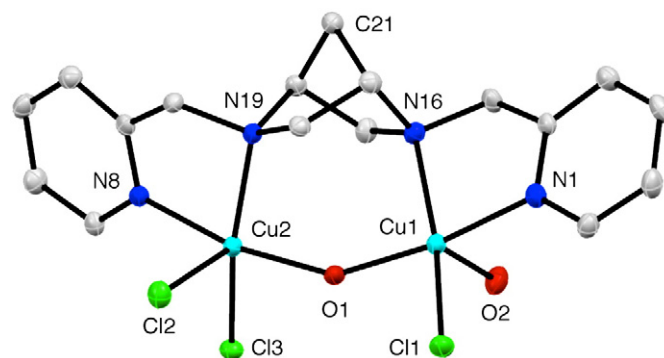


Fig. 1. Mercury diagram of **3** at the 50% probability level; hydrogen atoms and two molecules of water are omitted for clarity. Selected bond lengths (Å), and angles (°): Cu1–O1 1.918(2), Cu2–O1 1.937(2), Cu1–Cl1 2.298(1), Cu1–O2 2.200(2), Cu1–N1 2.015(2), Cu1–N16 2.091(2), Cu2–Cl2 2.529(1), Cu2–Cl3 2.295(1), Cu2–N8 2.025(2), Cu2–N19 2.084(2); Cu1–O1–Cu2 148.61(11), O1–Cu1–N1 171.24(9), O1–Cu1–N16 90.09(8), O1–Cu1–O2 97.46(8), O1–Cu1–Cl1 89.68(6), N1–Cu1–N16 82.39(9), N1–Cu1–O2 87.59(8), N1–Cu1–Cl1 95.77(6), N16–Cu1–O2 94.05(8), N16–Cu1–Cl1 159.42(6), O2–Cu1–Cl1 106.38(6), O1–Cu2–N8 167.11(8), O1–Cu2–N19 89.99(8), O1–Cu2–Cl2 96.86(6), O1–Cu2–Cl3 90.23(6), N8–Cu2–N19 81.03(8), N8–Cu2–Cl2 93.70(6), N8–Cu2–Cl3 94.50(6), N19–Cu2–Cl2 99.22(6), N19–Cu2–Cl3 157.27(6), Cl2–Cu2–Cl3 103.32(2).

is not as informative as for **1** and **2** due to the lack of acetate ligands, but nevertheless confirmed the presence of the ligands with a pyridyl C=N band at 1474 cm^{-1} for **3**, and a benzimidazolyl C=N band at 1617 cm^{-1} for **4**. Both complexes are EPR silent at room temperature and 77 K except for small signals that were attributed to paramagnetic (monomeric) impurities; this is consistent with antiferromagnetic coupling between the two $S = \frac{1}{2}\text{ Cu}^{2+}$ ions. Ultimately, complex **3** was characterized in the solid state by X-ray crystallography, confirming its bimetallic nature. Single crystals were obtained in the chiral space group $P2_1$ from a concentrated MeOH/H₂O solution by slow evaporation, with one molecule of **3** and two molecules of water present in the asymmetric unit. The symmetry of the ligand is reflected in the complex, which has a pseudo- C_2 axis passing through the bridgehead C21 and the hydroxo O1 atoms; lack of a strict C_2 -symmetry is due to the presence of one molecule of water as ligand towards Cu2 instead of the anionic chloride bound to Cu1 (Fig. 1). The coordination geometry around each cupric ion is square pyramidal with a slight distortion; in the case of Cu1, the square pyramid is defined by N1, N16, O1, and Cl1 as basal ligands, and a molecule of water (O2) in the axial position. Cu2 has a similar coordination environment defined by N8, N19, O1, and Cl3 in basal positions, and Cl2 in the axial position [11].

Introduction of 2-methylpyridyl and 1-methyl-2-methylbenzimidazolyl groups to (1*S*,4*S*)-2,5-diazabicyclo[2.2.1]heptane was reported in a biphasic CH₂Cl₂/H₂O system to afford **L**¹ and **L**² in good yields (Scheme 1). Replacement of the diazabicyclo with piperazine in the above procedure resulted in the achiral analogues **L**³ and **L**⁴ [12]. Initial characterization by ¹H NMR spectroscopy confirmed the presence of the signals corresponding to the piperazine framework, with a broad singlet at δ 2.47 and 2.54 ppm for **L**³ and **L**⁴, respectively. Singlets consistent with methylene groups were observed at δ 3.57 and 3.81 ppm, while an additional signal at 3.86 ppm was attributed to the benzimidazole *N*-methyl resonance of **L**⁴; in contrast, the methylene signals of the pendant 2-pyridyl and 2-benzimidazolyl groups of chiral **L**¹ and **L**² give rise to diastereotopic signals with geminal coupling ($J = 14.30$ and 13.35 Hz). Finally, the aromatic signals of the pyridyl and benzimidazolyl groups were observed between δ 7.01–8.45 and 7.25–7.76 ppm for **L**³ and **L**⁴. Electron-ionization mass spectrometry and IR spectroscopy confirmed the identity of the achiral ligands. The former technique revealed peaks at $m/z = 268$ and 374 ; the latter is characterized by a pyridyl C=N band at 1484 cm^{-1} for **L**³, and a benzimidazolyl C=N band at 1612 cm^{-1} for **L**⁴.

A contrasting behavior of the piperazine-derived ligands **L**³ and **L**⁴ was initially inferred from ESI-MS measurements in the reactions with 2 equivs. of CuCl₂. The ethanolic mixtures gave rise apparently to monometallic complexes detected at $[(\text{L}^3)\text{CuCl}]^+$ at $m/z = 366$, and $[(\text{L}^4)\text{CuCl}]^+$ at $m/z = 472$. Nonetheless, the isolated complexes were formulated as the bimetallic species $[(\text{L}^3)(\text{CuCl}_2)_2]$ (**5**) and $[(\text{L}^4)(\text{CuCl}_2)_2]$ (**6**) based on combustion analysis [13]. Solution EPR data were obtained

in H₂O for **5** and DMSO for **6** due to their poor solubility in less polar organic solvents. Partial solvolysis of the complexes may occur under these conditions, giving rise to the observed spectra consistent with isolated Cu²⁺ centers in axial environments ($g = 2.07$ and $g_{\parallel} = 2.24$ for **5**; $g = 2.20$ and $g_{\parallel} = 2.04$ for **6**). This observation is indicative of oligomeric or polymeric structures in the solid state, as confirmed for **5** by X-ray crystallography. Slow evaporation of a concentrated MeOH/H₂O solution gave rise to single crystals that revealed a polymeric structure $[(\text{L}^3)(\text{CuCl})_2(\mu\text{-Cl})_2]_n$. Complex **5** crystallizes in the triclinic space group $P-1$, with one half of the molecule generated by the center of symmetry. The piperazine backbone adopts a chair conformation, resulting in a distal arrangement of pyridine fragments, with N1 and the symmetry-related N1* donor atoms facing in opposite directions (Fig. 2). This geometric arrangement gives rise to a complex where two cupric ions are bound to two bidentate clefts on opposite sides of the piperazine, with a Cu··Cu distance of 6.886(1) Å that does not accommodate a bridging hydroxo ligand as observed for the chiral analogues **1–4**. Bridging interactions through Cl2 are present, generating a coordination polymer as depicted in Fig. 2 that results in pentacoordinate Cu²⁺ ions bound to the pyridine N1, N8, the terminal Cl1 ligand, and the bridging Cl2 and symmetry-related Cl2* ligands; in the polymer the Cu–Cu distance is 3.568(1) Å. The coordination geometry around Cu1 is best described as a distorted square pyramid ($\tau = 0.31$) [14].

Oxidative phenol coupling. 2,4-di-*tert*-butylphenol has been extensively used as a model substrate in oxidative C–C coupling reactions. This served as a test of the reactivity of the bimetallic complexes **1–6**. A general procedure was applied for all cupric complexes as potential catalysts: 5 or 10% mol of the complexes was added to 1 mmol of the phenol in 15 mL of acetonitrile; compressed air was bubbled through the solutions for several hours, and the progress was monitored by TLC (Scheme 2). Acetate-containing complexes **1** and **2** were the most active, with phenol consumed after 4 h; **3** and **4** required longer reaction times, and not all of the phenol was consumed even after bubbling with pure O₂ for 4 h; finally, the achiral complexes **5** and **6** failed to react with the phenol. In all cases the isolated product corresponded to the biphenol in Scheme 2, which forms by oxidative C–C coupling at the available phenolic *ortho*-C–H bond; the biphenol was characterized by ¹H NMR spectroscopy and IE-MS. Apparently, the hydroxo-bridged bimetallic core is required for oxidative C–C coupling to occur in these systems, highlighting the importance of not only the chiral nature of **L**¹ and **L**², but also their capability to induce dicopper complex formation. Initial reactivity tests for the oxidative C–C coupling of 2-naphthol

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