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Aerobic Oxidative Coupling of 2-Naphthol Derivatives Catalyzed by a Hexanuclear Bis(μ-hydroxo)copper(II) Catalyst

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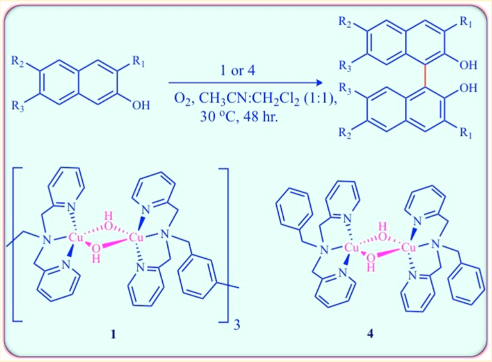
S *Supporting Information*

ABSTRACT: A novel hexanuclear bis(μ-hydroxo)copper(II) complex, $[\mathbf{L}_3(Cu_2(\mu\text{-}OH)_2)_3](ClO_4)_6$ (**1**), was synthesized with dinucleating ligand *N,N,N,N*-tetra(pyridin-2-ylmethyl)-*m*-xylene diamine (**L**). Complex **1** is fully characterized by X-ray crystallography and magnetic susceptibility in the solid state and UV−vis and electron paramagnetic resonance spectroscopy in solution. The molecular structure of **1** possesses three dicopper cores, in which two copper centers are bridged by two hydroxide groups and separated by a distance ranging from 2.8852(15) to 2.8937(10) Å. In addition, the three dicopper cores are linked by the dinucleating ligand between each pair of adjacent dicopper cores. Importantly, aerobic oxidative coupling of 2,4-di-*tert*-butylphenol, 2-naphthol, and six 2-naphthol derivatives was achieved in 33−96% yield using complex **1** as a catalyst.



INTRODUCTION

The activation of O_2 by copper ions is an important process in industrial manufacture and biological systems.[1] The binding of O_2 and its structure−reactivity relationships of the dinuclear copper enzymes, such as tyrosinase, catechol oxidase, and their model complexes, have been extensively investigated.[2] It is well-known that the reaction of copper(I) complexes with O_2 gives a stable bis(μ-hydroxo)dicopper(II) product.[3] The development of bis(μ-hydroxo)dicopper(II) complexes and their use in a catalytic oxidation by O_2 are topics of intense interest, because O_2 is abundant and an ecologically benign oxidant. On the other hand, the oxidative coupling of phenols to dimeric products, which has found extensive applications in chemical synthesis, catalyzed by copper complexes is a useful procedure.[4] Recently, Tolman et al. reported $[Cu_3O_2]^{3+}$ complexes that could react with 2,4-di-*tert*-butylphenol to form coupled product 3,3′,5,5′-tetra-*tert*-butyl-2,2′-biphenol in high yield (>97%).[5] Also, the similar oxidation of phenols reported by Itoh et al. using a (μ-η^2:η^2-peroxo)dicopper(II) or bis(μ-oxo)dicopper(III) complex gave isolated coupling products in ~50% yield based on the $[Cu_2/O_2]^{2+}$ complexes.[6] In addition, other transition metal complexes, such as Fe^{III},[7] Mn^{III},[8] Ti^{IV},[9] Ru^{II},[10] and V^{IV},[11] have been used as oxidants to promote the oxidative coupling of 2-naphthols; however, these methods suffer from difficulty in isolating the coupling product and a waste disposal problem. Meanwhile, an aerobic oxidative coupling of 2-naphthols catalyzed by amine-coordinated copper(II) complexes has been shown to be very effective and provided several promising results.[12] Recently, Kozlowski and co-workers designed a series of copper complexes of 1,5-diaza-*cis*-decalin diamines (N2s) and used them to promote the catalysis of the oxidative couplings of 3-substituted 2-naphthols under aerobic conditions. As the crystalline 2:1 diamine:copper complex $[(N2)Cu]Cl_2$ was employed in oxidative catalysis, no biaryl product was observed. The same reaction performed by using *in situ*-generated 1:1 N2:copper complex $[(N2)Cu(OH)]_3Cl_3$, found to be trimeric, as a catalyst (10 mol %) produced 1,1′-bi-2-naphthols (BINOLs) in 85% yield.[13] Therefore, there is still a strong demand for catalytic oxidative coupling of 2-naphthols to BINOLs under aerobic conditions and in the absence of additives.

Herein, we report the synthesis and detailed characterization of a novel hexanuclear bis(μ-hydroxo)copper(II) complex, $[\mathbf{L}_3(Cu_2(\mu\text{-}OH)_2)_3](ClO_4)_6$ (**1**), supported by dinucleating ligand *N,N,N,N*-tetra(pyridin-2-ylmethyl)-*m*-xylene diamine (**L**), and its catalytic ability with respect to the aerobic biaryl coupling of substituted phenols and 2-naphthols without any additives.

RESULTS AND DISCUSSION

Synthesis and X-ray Structure. Hexanuclear bis(μ-hydroxo)copper(II) complex $[\mathbf{L}_3(Cu_2(\mu\text{-}OH)_2)_3](ClO_4)_6$ (**1**) was synthesized from the reaction of $Cu(ClO_4)_2{\cdot}6H_2O$ with dinucleating ligand **L**. Ligand **L**, one methylene shorter than *m*-XYLpy$_2$[14] on a pyridyl N donor, was prepared by utilizing a

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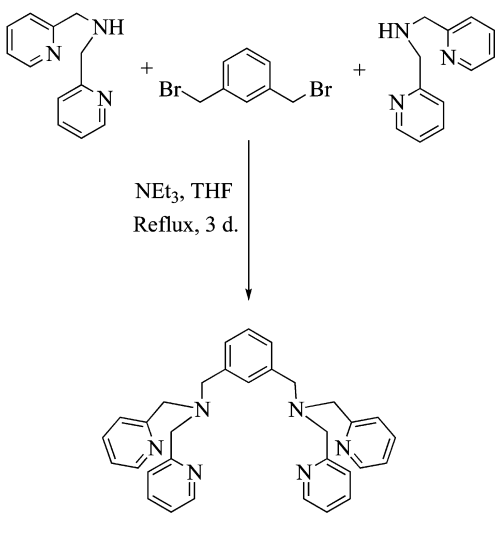
literature method.[15] The reaction of secondary amine bis(2-pyridylmethyl)amine with 1,3-dibromoxylene in tetrahydrofuran (THF) in the presence of triethylamine afforded **L** in nearly quantitative yield (Scheme 1) and in a highly pure form, which was confirmed by thin layer chromatography and nuclear magnetic resonance (NMR) spectroscopy.[15] To synthesize hexanuclear bis(μ-hydroxo)copper(II) complex **1**, a dicopper(II) complex, [**L**$(Cu(CH_3CN)_2)_2](ClO_4)_4$ (**2**), was prepared first by adding **L** to 2 equiv of $Cu(ClO_4)_2\cdot 6H_2O$ in CH_3CN under a N_2 atmosphere. The reaction mixture was transformed into a blue solution. The resulting solution was stirred for 1 h followed by removal of the solvent under vacuum. The resulting blue residue after washing with THF was redissolved in a small amount of CH_3CN, which allowed slow diffusion of Et_2O into the CH_3CN solution to yield X-ray quality crystals of **2**. Addition of 2 equiv of NaOH, predissolved in a CH_3CN/H_2O mixed solvent, to complex **2** afforded a pale blue solution of **1** (Scheme 2). After isolation and recrystallization by slow diffusion of Et_2O into the CH_3CN solution of **1**, sky blue crystals suitable for X-ray analysis were obtained over a week. Alternatively, hexanuclear bis(μ-hydroxo)copper(II) complex **1** could also be prepared from a copper(I) complex, [**L**$(CuCH_3CN)_2](ClO_4)_2$ (**3**). Complex **3** was synthesized by reacting 2 equiv of $[Cu(CH_3CN)_4](ClO_4)$ with 1 equiv of **L** in a THF/CH_3CN (2:1) mixed solvent at room temperature under a N_2 atmosphere. To determine the structure of cationic [**L**$(CuCH_3CN)_2]^{2+}$, counterion ClO_4^- of **3** was changed to PF_6^- by adding an aqueous solution (5 mL) of NH_4PF_6 to a CH_3CN solution of **3**. Bubbling O_2 into a wet CH_3CN solution of complex **3** would afford the entitled hexanuclear bis(μ-hydroxo)copper(II) complex **1** (Figure 1), which was confirmed by X-ray crystallography after recrystallization from an Et_2O/CH_3CN mixed solvent. In addition, a bis(μ-hydroxo)dicopper(II) complex, $[L'_2Cu_2(\mu\text{-}OH)_2](ClO_4)_2$ (**4**) [L′ = *N,N*-bis(2-pyridylmethyl)benzylamine], was prepared according to a literature method for spectroscopic and reactivity comparison with complex **1**.[16]

Scheme 1. Synthesis of Dinucleating Ligand L



L

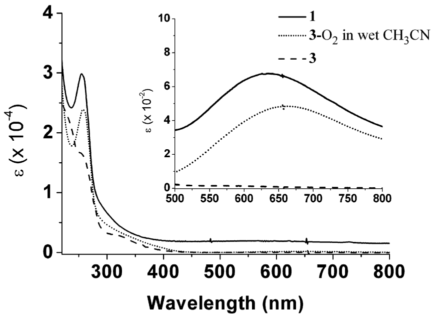
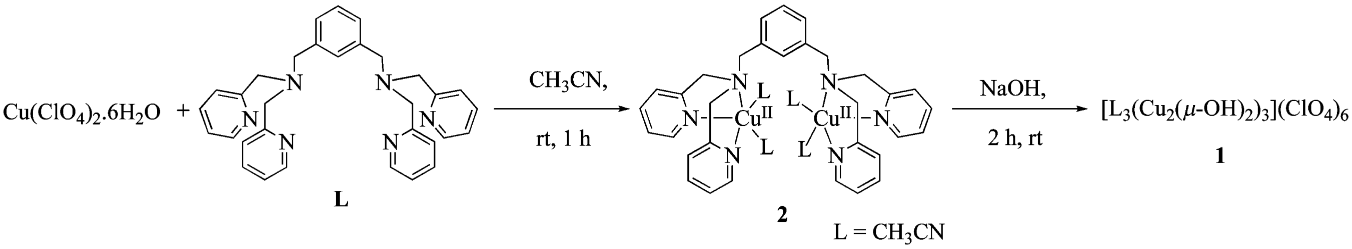
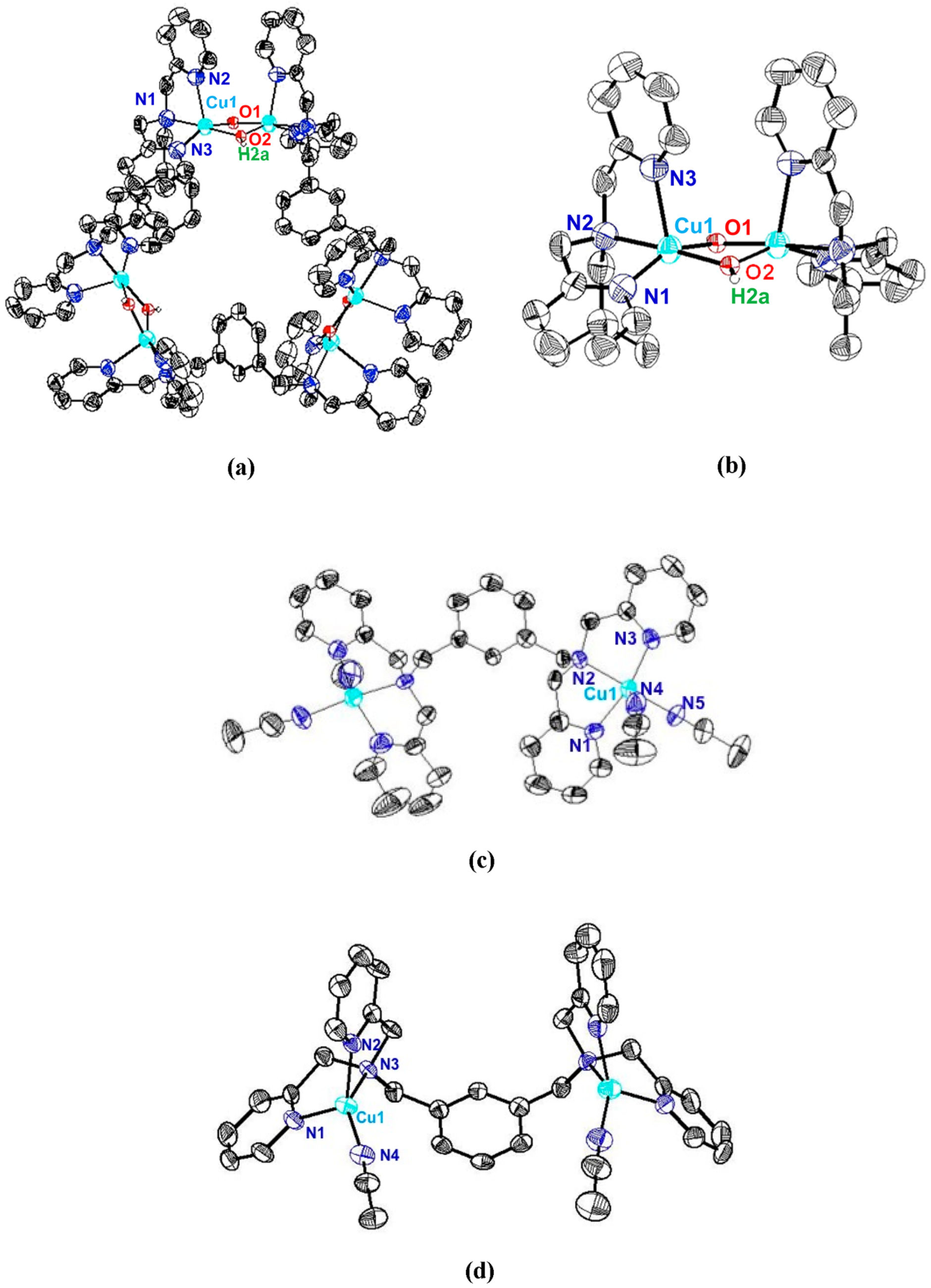


Figure 1. Comparison of UV−vis spectra of $[L_3(Cu_2(\mu\text{-}OH)_2)_3](ClO_4)_6$ (**1**) and reactions with **3**-O_2 and water.

The X-ray structural analysis reveals that complex **1** possesses three dicopper cores, in which two copper centers are bridged by two hydroxide groups, three linkers of the dinucleating **L** ligand between adjacent dicopper cores (Figure 2a), and six perchlorate anions. Each copper ion is coordinated by one amine N and two pyridyl N donors of **L** and two bridging hydroxide groups forming a five-coordinated distorted square pyramidal geometry (τ = 0.39).[17] For the coordination of the tridentate N3 donor of **L** in **1** wrapping around the copper ion, one pyridyl N_{py1} is bound axially and the amine N_{am} and the other pyridyl N_{py2} are bound equatorially. The hydroxide-bridged Cu⋯Cu distances range from 2.8852(15) to 2.8937(10) Å, and the two bridging hydroxide O atoms are separated by 2.51−2.52 Å. For five-membered chelate rings, the N−Cu−N angles [N_{am}−Cu−N_{py1}, 76.6(2)−78.9(2)°; N_{am}−Cu−N_{py2}, 82.0(2)−83.4(2)°; and N_{py1}−Cu−N_{py2}, 102.4(2)−104.12(19)°] are typical for this type of five-membered copper chelate.[18] The coordination of **L** in complexes **2** and **3** is similar to that of **1**. However, each copper ion is bound to two molecules of CH_3CN instead of two bridging hydroxide groups in **2** (Figure 2c) and one molecule of CH_3CN in complex **3** (Figure 2d). The distance between two copper ions in complex **2** (9.91 Å) is larger than that in complex **3** (7.88 Å). The hydroxide-bridged Cu⋯Cu distances of **1** are similar to those of the dinuclear copper(II) complexes previously reported by Manzur et al.,[16] which have OH^-, RO^-, F^-, or Cl^- as a bridging ligand. The selected bond lengths and angles of **1**−**3** are listed

Scheme 2. Synthesis of $[L_3(Cu_2(\mu\text{-}OH)_2)_3](ClO_4)_6$ (1)





(a) (b) (c) (d)

Figure 2. ORTEP representations of (a) $[\mathbf{L}_3(Cu_2(\mu\text{-}OH)_2)_3](ClO_4)_6$ (**1**), (b) the dicopper core of **1**, (c) $[\mathbf{L}(Cu(CH_3CN)_2)_2](ClO_4)_4$ (**2**), and (d) $[\mathbf{L}(CuCH_3CN)_2](PF_6)_2$ (**3**) showing 50% probability thermal ellipsoids. Hydrogen atoms and counteranions have been omitted for the sake of clarity.

in Table 1, and their crystal data and structural refinement statistics are listed in Table 2.

UV−Vis and Electron Paramagnetic Resonance (EPR) Spectroscopy of 1 and 4. The UV−vis spectra of bis(μ-hydroxo)copper(II) complexes **1** and **4** were recorded in CH_3CN and displayed an intense absorption band (257 nm, ε = 29850 M^{-1} cm^{-1} for **1**; 258 nm, ε = 9690 M^{-1} cm^{-1} for **4**) and a weak d−d transition band (634 nm, ε = 670 M^{-1} cm^{-1} for **1**; 654 nm, ε = 207 M^{-1} cm^{-1} for **4**) (Figure 3). EPR spectroscopy was employed to study the electronic behavior of complexes **1** and **4** in solution. The EPR measurements for both copper(II) complexes **1** and **4** were performed in frozen CH_3CN at 77 K (Figure 4). The spectra revealed typical axial spectra[19] with the observed values of $g_{\parallel}$ (2.258 for **1** and 2.223 for **4**) being greater than the values of $g_{\perp}$ (2.064 for **1** and 2.061 for **4**) with hyperfine coupling constants $A_{\parallel}$ (180 G for **1** and 176 G for **4**). Unlike many reported complexes possessing a bis(μ-hydroxo)dicopper(II) core,[2d,19d,20] in which a strong antiferromagnetic coupling between two copper(II) ions would occur and result in an EPR silent signal in the frozen solution, the EPR spectra of **1** and **4** in frozen CH_3CN are typical axial spectra for distorted square pyramidal complexes with a mononuclear copper(II) center having a $d_{x^2-y^2}$ ground state.[21] This result suggests that the exchange coupling between two copper ions in the bis(μ-hydroxo)dicopper(II) core of **1** and **4** is a weak antiferromagnetic interaction, which was clearly shown in the magnetic studies.

Table 1. Selected Bond Lengths (angstroms) and Angles (degrees) for Complexes 1−3

	1	2	3
Cu1···Cu2	2.8937(10)	−	−
Cu3···Cu3′	2.8852(15)	−	−
Cu1−O1	1.927(4)	−	−
Cu1−O2	1.960(4)	−	−
Cu2−O1	1.956(4)	−	−
Cu2−O2	1.902(4)	−	−
Cu3−O3	1.910(4)	−	−
Cu3−O3′	1.934(5)	−	−
Cu1−N1	2.001(5)	1.978(5)	2.048(5)
Cu1−N2	2.052(5)	2.026(5)	2.243(5)
Cu1−N3	2.228(5)	1.971(5)	2.050(6)
Cu1−N7	−	2.344(6)	1.912(6)
Cu1−N9	−	1.975(6)	−
Cu2−N4	2.249(5)	1.978(6)	2.074(6)
Cu2−N5	2.039(5)	2.036(5)	2.238(5)
Cu2−N6	1.985(5)	1.986(5)	2.023(6)
Cu2−N8	−	2.002(6)	1.876(7)
Cu2−N10	−	2.315(7)	−
Cu3−N11	1.981(7)	−	−
Cu3−N12	2.056(5)	−	−
Cu3−N13	2.269(5)	−	−
N1−Cu1−N2	83.4(2)	83.29(19)	81.20(19)
N2−Cu1−N3	78.9(2)	82.4(2)	78.8(2)
N1−Cu1−N3	104.12(19)	165.6(2)	118.3(2)
N4−Cu2−N5	76.6(2)	82.5(2)	80.0(2)
N5−Cu2−N6	82.0(2)	82.77(19)	80.4(2)
N4−Cu2−N6	103.0(2)	164.7(2)	120.6(2)
N11−Cu3−N12	82.1(3)	−	−
N12−Cu3−N13	77.2(2)	−	−
N11−Cu3−N13	102.4(2)	−	−
O1−Cu1−O2	80.89(16)	−	−
O1−Cu2−O2	81.61(16)	−	−
O3−Cu3−O3′	81.51(19)	−	−
Cu1−O1−Cu2	96.35(17)	−	−
Cu1−O2−Cu2	97.04(18)	−	−
Cu3−O3−Cu3′	97.30(19)	−	−

Magnetic Properties of Bis(μ-hydroxo)copper(II) Complexes 1 and 4. Magnetic susceptibility χ for both bis(μ-hydroxo)copper(II) complexes **1** and **4** has been obtained in the solid state over the temperature range of 2−300 K. The plots of χ versus T (left) and $1/\chi$ versus T (right) for complexes **1** and **4** are shown in panels a and b of Figure 5, respectively. The χ data follow Curie−Weiss behavior for both complexes. No signature of long-range ordering (LRO) was seen down to 2 K. The experimental data were fit to Curie−Weiss law $\chi(T) = \chi_0 + C/(T - \theta_{CW})$ over temperature ranges of 30−300 K for complex **1** and 20−300 K for complex **4**, where χ_0 is the temperature-independent susceptibility, the sum of diamagnetic susceptibility (χ_{dia}) and Van-Vleck susceptibility (χ_{vv}), C is the Curie constant, and θ_{CW} is the Curie−Weiss temperature. The values resulting from the Curie−Weiss fit are listed in Table 3. The value of C for complex **1** is inconsistent with the value of C expected for $S = {}^1/_2$ spin (1.73 μ_B) systems, whereas the value of C of complex **4** is slightly larger than 1.73 μ_B, suggesting the effect of weak spin−orbit coupling in complex **4**. The negative values of θ_{CW} for complexes **1** and **4** (−10 and −1 K, respectively) suggest that the exchange interactions between two copper(II) ions are weak antiferromagnetic coupling. This result can also be found in the insets of panels a and b of Figure 5, which illustrates clearly that μ_{eff} is affected and falls below $T < \theta_{CW}$ for the respective complexes **1** and **4**. Because the Cu−O−Cu bond angles in the bis(μ-hydroxo)dicopper core for complexes **1** and **4** are in the range of 96−98, weak antiferromagnetic couplings are expected according to Goodenough−Kanamori rules.[22] The presence of weak antiferromagnetic coupling in complexes **1** and **4** is also evidenced by their EPR spectra (Figure 4).

Catalytic Activity of 1 and 4. Many model complexes for copper enzymes, such as tyrosinase and catechol oxidase, have shown the reactivity for coupling of phenols.[23] More interestingly, the reaction of (μ-η^2:η^2-peroxo)dicopper(II) complexes with phenols afforded C−C coupling biphenols rather than catechols, the oxygenation products.[6,23,24] On the basis of this idea, we are inspired to examine the reactivity of bis(μ-hydroxo)copper(II) complexes **1** and **4**. Initially, an aerobic oxidative coupling of 2,4-di-*tert*-butylphenol was performed as a reference to shed light on the role of the catalytic activity of complexes **1** and **4** (Scheme 3). The reaction proceeded smoothly and gave 3,3′,5,5′-tetra-*tert*-butyl-2,2′-biphenol rather than 3,5-di-*tert*-butylcatechol in CH_3CN at 30 °C for 48 h under 1 atm of O_2 with 2 mol % loading of catalyst in good yield (75% for **1** and 49% for **4**). With this success, aerobic oxidative couplings of 2-naphthol using complexes **1**, **2**, and **4** and copper salts, such as $CuSO_4$, $CuCl_2$, and $Cu(ClO_4)_2$, as catalysts under the same aerobic condition were further studied. While all employed copper salts and complex **2** showed very poor oxidation catalysis, only complexes **1** and **4** exhibited good catalytic activity [84% yield for 2 mol % **1** and 82% yield for 6 mol % **4** (Table 4, entries 7 and 10)]. The reaction also proceeded at 40 and 60 °C and was found to produce no increase in yield. However, if DMF was used as the reaction solvent, conversion of 2-naphthol to 1,1′-bi-2-naphthol (BINOL) declined to a 63% yield, and an even lower yield of 43% using MeOH as a solvent for complex **1** (Table 4, entries 8 and 9, respectively), and the yield was reduced to 55% with DMF and 32% with MeOH in the case of complex **4** (Table 4, entries 12 and 14, respectively).

Having obtained bis(μ-hydroxo)copper(II) complexes **1** and **4** as the catalysts for aerobic oxidative coupling of 2-naphthol in good yields under mild conditions, we explored the coupling reactions in mixed solvents under similar aerobic conditions (Table 5). To our surprise, conversion of 2-naphthol to BINOL using a $CH_3CN/MeOH$ (4:1) mixed solvent gave 26% yield, which increased to 69−82% in various mixed solvents using 2 mol % loading of catalyst **1** (Table 5, entries 1−5). Similarly, the yield was promoted using mixed solvents with 2 mol % loading of catalyst **4** for the same reaction (Table 5, entries 11−13). These results revealed that a mixed solvent, CH_3CN/CH_2Cl_2 (4:1), for an aerobic oxidative coupling of 2-naphthol would increase the yield of the reaction more than a single solvent alone. We have also performed the reaction using 1 mol % catalyst **1** in a CH_3CN/CH_2Cl_2 (4:1) mixed solvent, and the yield was slightly reduced to 73% (Table 5, entry 6). As the ratio of the mixed solvent (CH_3CN/CH_2Cl_2) changed to 2:1, the yield was increased to 85% (Table 5, entry 7) in the case of catalyst **1** and increased from 74 to 81% with 2 mol % catalyst **4** (Table 5, entries 13 and 14, respectively). In light of this observation, the reaction conditions for the formation of BINOL were optimized by varying the $CH_3CN:CH_2Cl_2$ ratio with the usage of 1 mol % catalyst **1**. The yield was increased to 88% when a 1:1 $CH_3CN:CH_2Cl_2$ ratio was used. With a further

Table 2. Crystal Data and Structural Refinement Statistics for 1−3

	1	2	3
molecular formula	$C_{96}H_{102}Cl_6Cu_6N_{18}O_{31}$	$C_{40}H_{44}Cl_4Cu_2N_{10}O_{16}$	$C_{36}H_{38}Cu_2F_{12}N_8P_2$
formula weight	2597.90	1189.73	999.76
temperature (K)	200(2)	200(2)	200(2)
wavelength (Å)	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	triclinic
space group	*C*2/*c*	*P*21/*c*	$P\bar{1}$
a (Å)	16.5608(5)	9.0132(3)	11.2980(16)
b (Å)	34.7656(8)	31.3362(9)	12.948(3)
c (Å)	23.6980(6)	18.9321(5)	17.812(4)
α (deg)	90	90	106.601(14)
β (deg)	90.063(2)	96.4750(10)	98.692(14)
γ (deg)	90	90	99.664(9)
volume ($Å^3$)	13644.0(6)	5313.1(3)	2406.4(8)
Z	4	4	2
density (calcd) (Mg/m^3)	1.265	1.487	1.380
absorption coefficient (mm^{-1})	1.105	1.075	1.030
F(000)	5312	2432	1012
crystal size (mm^3)	0.52 × 0.36 × 0.30	0.52 × 0.39 × 0.22	0.46 × 0.38 × 0.07
θ range (deg)	1.17−25.06	2.26−25.00	1.74−25.19
no. of reflections collected	47823	30061	19981
no. of independent reflections	11739 (R_{int} = 0.0471)	9322 (R_{int} = 0.0530)	8483 (R_{int} = 0.0994)
completeness to θ (%)	97.1	99.6	98.0
absorption correction	multiscan	multiscan	multiscan
maximal/minimal transmission	0.7329 and 0.5974	0.7979 and 0.6049	0.9314 and 0.6487
data/restraints/parameters	11739/0/668	9322/0/587	8483/0/506
goodness of fit on F_2	1.073	1.037	0.905
final R1 and wR2 indices [$I > 2\sigma(I)$]	0.0780, 0.2351	0.0771, 0.2078	0.0849, 0.2050
R1 and wR2 indices (all data)	0.1099, 0.2538	0.1077, 0.2217	0.1509, 0.2352
largest difference peak and hole (e $Å^{-3}$)	1.186 and −0.858	0.712 and −0.741	1.134 and −0.697

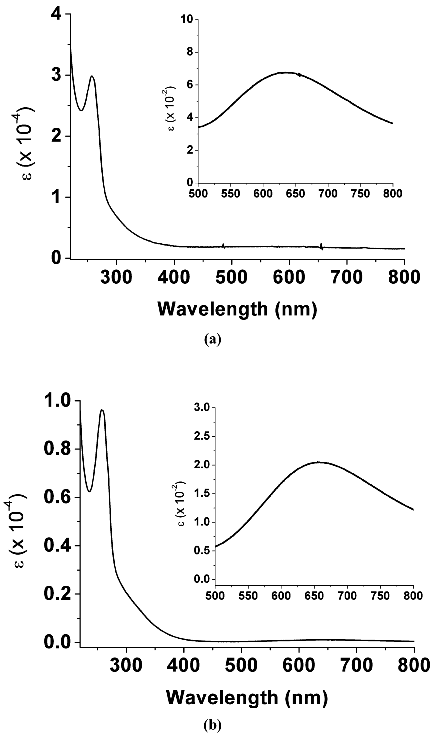


Figure 3. UV−vis spectra of (a) $[L_3(Cu_2(\mu\text{-}OH)_2)_3](ClO_4)_6$ (**1**) and (b) $[L'_2Cu_2(\mu\text{-}OH)_2](ClO_4)_2$ (**4**) in CH_3CN. The inset shows the intensity of the d−d band.

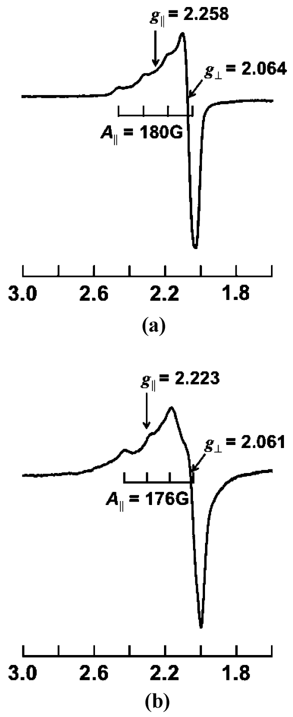
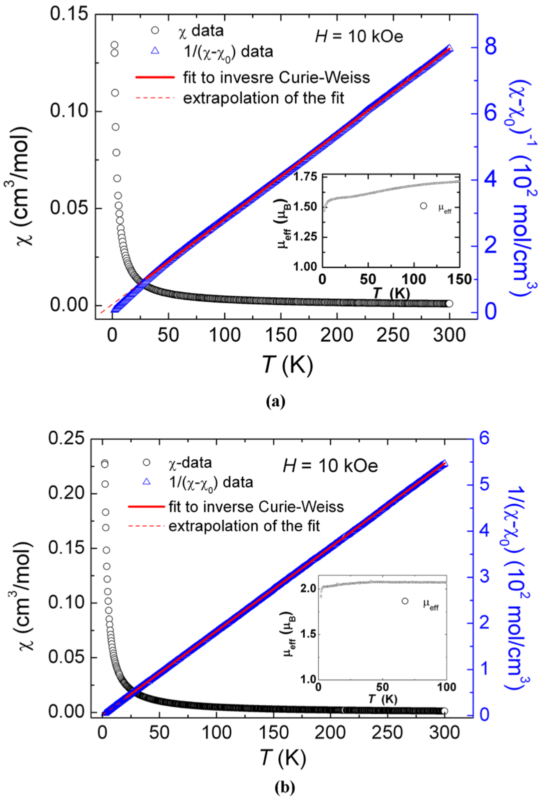


Figure 4. X-Band EPR spectra of (a) $[L_3(Cu_2(\mu\text{-}OH)_2)_3](ClO_4)_6$ (**1**) and (b) $[L'_2Cu_2(\mu\text{-}OH)_2](ClO_4)_2$ (**4**) in CH_3CN.

increase in the quantity of CH_2Cl_2 (1:2 CH_3CN:CH_2Cl_2 ratio), the yield decreased to 82% and further decreased to 74% when



(a)

(b)

Figure 5. Magnetic susceptibility of (a) $[\mathbf{L}_3(Cu_2(\mu\text{-}OH)_2)_3](ClO_4)_6$ (**1**) and (b) $[\mathbf{L'}_2Cu_2(\mu\text{-}OH)_2](ClO_4)_2$ (**4**) (left) and inverse magnetic susceptibility (right) vs temperature in the solid state. The inset shows the plot of μ_{eff} vs T.

a 1:4 CH_3CN:CH_2Cl_2 ratio was used (Table 5, entries 8–10). A similar phenomenon was observed in the case of catalyst **4** (Table 5, entries 15–17).

Under the optimized conditions described above, oxidative couplings of several 2-naphthol derivatives were examined. Moderate yields were obtained in the reactions of 6-cyano- and 3-iodo-2-naphthols (Table 6, entries 3 and 6, respectively). Much to our delight, the reaction yield was 90% with 7-methoxy-2-naphthol was applied, 94% with 6-bromo-2-naphthol, and 96% with 6-phenyl-2-naphthol using 1 mol % catalyst **1** (Table 6, entries 7, 2, and 4, respectively).

■ CONCLUSIONS

Hexanuclear bis(μ-hydroxo)copper(II) complex **1** supported by a dinucleating ligand, *N*,*N*,*N*,*N*-tetra(pyridin-2-ylmethyl)-*m*-xylene diamine (**L**), has been successfully synthesized and was spectroscopically and structurally characterized. Notably, complex **1** can serve as a catalyst for the aerobic oxidative coupling of 2-naphthols to form BINOLs. The reaction proceeded smoothly via oxidative coupling rather than oxygenation under an O_2 atmosphere.

Scheme 3. Synthesis of 3,3′,5,5′-Tetrabutyl-1,1′-bi-2,2′-phenol

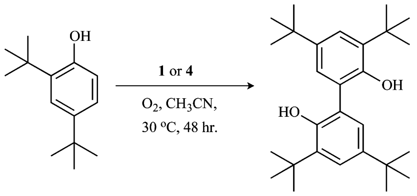
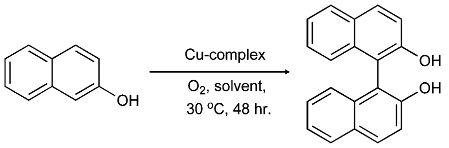


Table 4. Conversion of 2-Naphthol to BINOL Derivatives Using Various Cu^{II} Compounds



entry	Cu complex	solvent	yield (%)[a]
1	$Cu(ClO_4)_2$[b]	CH_3CN	5.4
2	$Cu(ClO_4)_2$[b]	DMF	3.3
3	$Cu(ClO_4)_2$[b]	MeOH	trace
4	**2**[c]	CH_3CN	trace
5	**2**[c]	DMF	trace
6	**2**[c]	MeOH	trace
7	**1**	CH_3CN	84[d] (75)[e]
8	**1**	DMF	63[c]
9	**1**	MeOH	43[c]
10	**4**	CH_3CN	82[f] (81),[g] (73),[h] (60)[h]
11	**4**	CH_2Cl_2	71[e]
12	**4**	DMF	55[e]
13	**4**	$(CH_3)_2CO$	53[e]
14	**4**	MeOH	32[e]

[a] Yield of the product isolated via column chromatography. [b] Reaction performed in 12 mol % **1**. [c] Reaction performed in 2 mol % **1**. [d] Reaction performed in 1 mol % **1**. [e] Reaction performed in 6 mol % **4**. [f] Reaction performed in 4 mol % **4**. [g] Reaction performed in 2 mol % **4**. [h] Reaction performed in 1 mol % **4**.

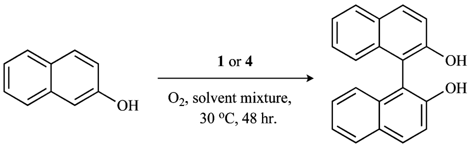
■ EXPERIMENTAL SECTION

General Information. All manipulations were performed under nitrogen using standard Schlenk and glovebox techniques. Methanol was dried in magnesium/iodine prior to use. Acetonitrile was distilled once from P_2O_5 and freshly distilled from CaH_2 before being used. Diethyl ether and THF were dried in a sodium benzophenone still prior to being used. α,α′-Dibromo-*m*-xylene, dipicolyl amine, 2,4-di-*tert*-butylphenol, 2-naphthol, 6-bromo-2-naphthol, 7-methoxy-2-naphthol, and 6-cyano-2-naphthol are commercially available and were used as received. UV–vis spectra were recorded on an absorption spectrophotometer. Infrared (IR) spectra were recorded using KBr pellets or the solution cell method. NMR spectra were recorded on a 400 MHz NMR spectrometer. EPR measurements were performed at the X-band using a spectrometer equipped with a superhigh-sensitivity cavity. Cu^{II} complexes **1** and **4** were dissolved in CH_3CN in a 2 mm EPR tube. The sample solutions were frozen with liquid nitrogen, and the X-band EPR spectra of **1** and **4** were recorded at 77 K with a microwave power of 15.000 mW (frequency of 9.6608 GHz, conversion time of ~2.048 ms). The magnetic susceptibility data

Table 3. Magnetic Susceptibility Data for Complexes 1 and 4

complex	T (K)	χ_0 (cm³/mol of Cu)	C [cm³ K^{-1} (mol of Cu)$^{-1}$]	μ_{eff} (μ_B)	θ_{CW} (K)
1	30–300	$-(3 \pm 0.1) \times 10^{-4}$	0.40	1.78	−10 (AF)
4	20–300	$-(5.5 \pm 0.1) \times 10^{-4}$	0.54	2.08	−0.7 (AF)

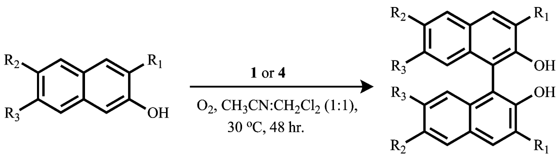
Table 5. Optimization of the Reaction Conditions for the Conversion of 2-Naphthol to BINOL



entry	catalyst	catalyst loading (mol %)	solvent	ratio	yield (%)[a]
1	**1**	2	CH_3CN/MeOH	4:1	26 (51)[b]
2	**1**	2	CH_3CN/DMF	4:1	69
3	**1**	2	CH_3CN/H_2O	4:1	70
4	**1**	2	CH_3CN/acetone	4:1	79
5	**1**	2	CH_3CN/CH_2Cl_2	4:1	82
6	**1**	1	CH_3CN/CH_2Cl_2	4:1	73
7	**1**	1	CH_3CN/CH_2Cl_2	2:1	85
8	**1**	1	CH_3CN/CH_2Cl_2	1:1	88
9	**1**	1	CH_3CN/CH_2Cl_2	1:2	82
10	**1**	1	CH_3CN/CH_2Cl_2	1:4	74
11	**4**	2	CH_3CN/DMF	4:1	60
12	**4**	2	CH_3CN/acetone	4:1	71
13	**4**	2	CH_3CN/CH_2Cl_2	4:1	74
14	**4**	2	CH_3CN/CH_2Cl_2	2:1	81
15	**4**	2	CH_3CN/CH_2Cl_2	1:1	86
16	**4**	2	CH_3CN/CH_2Cl_2	1:2	83
17	**4**	2	CH_3CN/CH_2Cl_2	1:4	75

[a] Yield of the product isolated via column chromatography. [b] Reaction performed under reflux conditions.

Table 6. Aerobic Oxidative Coupling of Various 2-Naphthols



entry	R_1	R_2	R_3	yield (%)[a] **1**[b]	yield (%)[a] **4**[c]
1	H	H	H	88	87
2	H	Br	H	94	74
3	H	CN	H	74	62
4	H	phenyl	H	96	84
5	COOMe	H	H	33	8
6	I	H	H	79	60
7	H	H	OMe	90	73

[a] Yield of the product isolated via column chromatography. [b] Reaction performed in 1 mol % complex **1**. [c] Reaction performed in 2 mol % complex **4**.

were obtained on powder samples of **1** and **4** using SQUID-VSM in the temperature range from 2 to 300 K, under a magnetic field (H) of 10 kOe. Electrospray ionization mass spectrometry spectra were recorded using a LCQ Advantage spectrometer. Elemental analyses for C, H, and N were recorded at the MST Regional Instrumental Center at National Taiwan University.

Determination of X-ray Structure. Crystals of a suitable size for the CCD X-ray diffractometer were selected under a microscope and mounted on the tip of a glass fiber fashioned on a copper pin. X-ray data for complexes **1**−**3** were collected on a CCD diffractometer employing graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) at 200 K in θ−2θ scan mode. The space groups for complexes were determined on the basis of systematic absences and intensity statistics, and the structures of **1**−**3** were determined by direct methods using SIR92 or SIR97 and refined using SHELXL-97. An empirical absorption correction by multiple scans was applied to both structures. All non-hydrogen atoms were refined with anisotropic displacement factors. Hydrogen atoms were placed in ideal positions and fixed with relative isotropic displacement parameters. Detailed crystallographic data of all complexes are provided as a CIF file.

Synthesis of *N,N,N,N*-Tetra(pyridin-2-ylmethyl)-*m*-xylene Diamine L. Bis(pyridin-2-ylmethyl)amine (0.9 g, 6.0 mmol) and triethylamine (0.83 mL, 6.0 mmol) were dissolved in 10 mL of THF in a 50 mL round-bottom flask and stirred for 10 min. A solution of α,α'-dibromo-*m*-xylene (0.8 g, 3.0 mmol) in 20 mL of THF was gradually added to the solution described above. The resulting mixture was refluxed at 80 °C for 72 h. The precipitate of $NEt_3\cdot HBr$ was filtered off, and the filtrate was rotary evaporated and pumped under vacuum to remove traces of solvent and Et_3N. The resulting solution was extracted with CH_2Cl_2 and washed with a brine solution. The CH_2Cl_2 solution was collected and dried over $MgSO_4$. Pure golden brown oil of **L** was obtained by column chromatography: yellow oil; 88%; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.49−8.47 (m, 4H), 7.71−7.67 (m, 4H), 7.58−7.52 (m, 5H), 7.25 (s, 3H), 7.22−7.18 (m, 4H), 3.76 (s, 8H), 3.66 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 159.5, 148.6, 138.7, 136.0, 128.9, 127.9, 127.3, 122.4, 121.6, 59.7, 58.2.

Synthesis of Hexanuclear Copper(II) Complex 1, $[L_3Cu_6(\mu\text{-}OH)_6](ClO_4)_6$. A degassed solution of polydentate ligand **L**, *N,N,N,N*-tetra(pyridin-2-ylmethyl)-*m*-xylene diamine (0.115 g, 0.25 mmol), was dissolved in 5 mL of CH_3CN and then transferred to a CH_3CN solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.185 g, 0.5 mmol) in a round-bottom flask under an inert atmosphere. The reaction mixture was stirred for 1 h at room temperature, and NaOH (0.02 g, 0.5 mmol) dissolved in a CH_3CN/H_2O mixed solvent was added to the reaction flask. The reaction mixture was stirred for an additional 2 h followed by removal of the solvent under vacuum. THF was added to the reaction mixture, resulting in a pale blue residue, which was redissolved in a small amount of CH_3CN and filtered through Celite to yield a clear pale blue solution. The filtrate was concentrated and transferred to a vial for crystallization by slow diffusion of diethyl ether into the concentrated CH_3CN solution of **1** at −20 °C over a week. Pale blue crystals were formed and isolated in 56% yield: IR (neat) 3433 (br, OH), 1617, 1439, 1375, 1287, 1094 cm^{-1} (vs, ClO_4^-). Anal. Calcd for $C_{96}H_{112}Cu_6N_{18}O_{35}Cl_6$: C, 43.15; H, 4.22; N, 9.44. Found: C, 42.81; H, 4.33; N, 9.40.

Synthesis of Dicopper(II) Complex 2, $[L(Cu(CH_3CN)_2)_2](ClO_4)_4$. A degassed solution of polydentate ligand **L**, *N,N,N,N*-tetra(pyridin-2-ylmethyl)-*m*-xylene diamine (0.115 g, 0.25 mmol), was dissolved in 5 mL of CH_3CN and then transferred to a CH_3CN solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.185 g, 0.5 mmol) in a round-bottom flask under an inert atmosphere. The reaction mixture was stirred for 2 h followed by removal of the solvent under vacuum. The resulting blue residue after being washed with THF was redissolved in a small amount of CH_3CN and filtered through Celite to yield a clear blue solution. The filtrate was concentrated and transferred to a vial for crystallization by the slow diffusion of diethyl ether into the concentrated CH_3CN solution of the product at −20 °C for a week. Blue crystals were formed and isolated in 73% yield: FAB-HRMS found 922.9722, calcd for $[C_{32}H_{32}Cl_3Cu_2N_6O_{12}]^+$ 922.9736; IR (neat) 3582 (sharp), 3427, 1616, 1478, 1443, 1287, 1094 cm^{-1} (vs, ClO_4^-). Bulk samples, even crystals, were sent for elementary analysis several times, but no good data were obtained. We suspect that the bound CH_3CN molecules are readily dissociated from the copper centers. The TGA data of **2** confirm this idea. The bound CH_3CN molecules start to dissociate from the copper centers at 40 °C (see Figure S1 of the Supporting Information). Therefore, the sample for elementary analysis lost the bound CH_3CN molecules before it entered the combustion chamber, and no good elementary analysis data for **2** were obtained.

Synthesis of Dicopper(I) Complex 3, $[L(CuCH_3CN)_2](ClO_4)_2$. A degassed solution of polydentate ligand **L**, *N,N,N,N*-tetra(pyridin-2-ylmethyl)-*m*-xylene diamine (0.25 g, 0.5 mmol), was dissolved in 5 mL of dry CH_3CN and then transferred to a THF solution of $Cu(CH_3CN)_4(ClO_4)$ (0.327 g, 1 mmol) in a round-bottom flask under an inert atmosphere. The reaction mixture was stirred for 2 h followed by removal of the solvent under vacuum. The resulting yellow residue after being washed with diethyl ether was redissolved in MeOH, and to the mixture was further added an aqueous solution (5 mL) of NH_4PF_6 (0.327 g, 2.01 mmol) to afford a yellow-green powder. The resulting suspension was dissolved by addition of CH_3CN (~3 mL) to give a yellow-green solution, to which diethyl ether was diffused at −20 °C to give yellow-green crystals. The crystals were collected by filtration and dried *in vacuo*: yield 0.513 g (97%); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.55−8.54 (m, 4H), 7.83−7.79 (m, 4H), 7.46 (s, 1H), 7.41−7.32 (m, 10H), 7.25−7.23 (m, 1H), 3.86 (s, 4H), 3.84 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 156.8, 149.0, 138.1, 135.5, 132.9, 130.6, 128.2, 124.1, 124.0, 60.1, 58.8. Anal. Calcd for $C_{36}H_{38}Cl_2Cu_2N_8O_8\cdot 2H_2O$: C, 45.77; H, 4.48; N, 11.86. Found: C, 45.85; H, 3.85; N, 12.09.

General Procedure for Aerobic Oxidative Coupling of 2-Naphthols. The typical procedure of oxidative coupling of 2-napthols with bis(μ-hydroxo)copper(II) complex **1** or **4** is described here. To a solution (4 mL) of 2-naphthol or its derivatives (1 mmol) was added bis(μ-hydroxo)copper(II) complex **1** or **4** (1 mol % for **1** and 2 mol % for **4**) at room temperature. After being stirred for 48 h, the reaction mixture was washed with water and a brine solution. The residue was purified by column chromatography on silica gel (4:1 hexane/ethyl acetate) to give the biaryl product. Characterizations of the C−C coupling biaryl products are listed in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional data and spectra and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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