Modeling Tyrosinase Monooxygenase Activity. Spectroscopic and Magnetic Investigations of Products Due to Reactions between Copper(I) Complexes of Xylyl-Based Dinucleating Ligands and Dioxygen: Aromatic Ring Hydroxylation and Irreversible Oxidation Products†

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A full account of a chemical system possessing features that mimic the reactivity aspects of tyrosinase is presented. Using dinucleating ligands with a *m*-xylyl spacer three new dicopper(I) complexes have been synthesized and their reactivity with dioxygen investigated. The six-membered chelate ring forming ligands provide only two nitrogen coordinations to each copper. The complexes $[Cu^{I}_2L(CH_3CN)_2]X_2$ (X = ClO_4^- (**1a**), SbF_6^- (**1b**)) and $[Cu^{I}_2(L\text{-}NO_2)(CH_3CN)_2][SbF_6]_2$ (**1c**) [L = α,α′-bis[*N*-methyl-*N*-(2-pyridylethyl)amino]-*m*-xylene; L-NO_2 = *para*-nitro derivative of L] have been characterized by IR and ^1H NMR spectroscopy. The reaction of O_2 with **1a**−**c** in CH_2Cl_2 or THF is instantaneous and causes stoichiometric xylyl hydroxylation reactions producing phenol products. Thus **1a** produces phenoxo-/hydroxo-bridged product $[Cu^{II}_2(L\text{-}O)(OH)][ClO_4]_2$ (**2a**). The existence of putative peroxo−dicopper(II) species could not be detected even at −80 °C. A trend is observed for the extent of aromatic ring hydroxylation (298 K): $CH_3CN \sim DMF > CH_3OH \gg CH_2Cl_2$. Cyclic voltammetric experiment of **1a** in DMF reveals an appreciably low redox potential ($E_{1/2}$ = −0.26 V vs SCE) for the Cu^{II}_2/Cu^{I}_2 redox process. Variable-temperature (25−300 K) magnetic susceptibility measurements establish that the copper(II) centers in **2a** and the dihydroxo-bridged complex $[Cu^{II}_2L'(OH)_2][ClO_4]_2$ (**2b**) [formed due to an impurity (L′) present during the synthesis of L following Method A; L′ = bis[α,α′-bis(*N*-methyl-*N*-(2-pyridylethyl)amino)-*m*-xylene]methylamine] are antiferromagnetically coupled, with **2a** considerably more coupled than **2b**. Reaction of **1a** with O_2 in CH_2Cl_2 (298 K) produces an additional unhydroxylated product of composition $[Cu^{II}_2L(OH)(OH_2)][ClO_4]_3 \cdot 2H_2O \cdot 0.5HCl$ (**3a**). In agreement with its proposed hydroxo-/aquo-bridged structure, **3a** is weakly antiferromagnetically coupled. In CH_3CN solution, **3a** rearranges to generate a doubly hydroxo-bridged species $[Cu^{II}_2L(OH)_2]^{2+}$. Using a solution-generated dicopper(I) complex of a closely similar ligand (L″) providing five-membered chelate ring, the reactivity toward dioxygen was also investigated. It produces only an irreversibly oxidized product of composition $Cu^{II}_2L''(OH)(ClO_4)_3(H_2O)_2$ (**3b**) (L″ = α,α′-bis[*N*-methyl-*N*-(2-pyridylmethyl)-amino]-*m*-xylene). For **3b** the copper(II) centers are almost uncoupled.

Introduction

The activation of molecular oxygen by copper plays a central role in synthetically useful stoichiometric and catalytic oxidative conversions of organic molecules and in biological systems.[1−6] Hemocyanin (Hc) and tyrosinase (Tyr) are dinuclear copper-containing proteins that bind or activate dioxygen. Hc functions as a dioxygen carrier, and Tyr, a monooxygenase, which hydroxylates monophenols (tyrosine) and further oxidizes the *o*-diphenol to an *o*-quinone. The structures of both deoxy and oxy forms of Hc have been determined by X-ray crystallography.[3,4] In oxyHc the presence of a novel (μ-η^2:η^2-peroxo)dicopper(II) species has been identified. This Cu_2O_2 unit provides a strong antiferromagnetic coupling in the binuclear site.[3] Each copper center has a distinctly elongated histidine coordination (Cu−N bond length 2.26 Å) above and below the $Cu-O_2-Cu$ plane and has two equatorial histidine coordinations (Cu−N bond length 2.00 Å). No X-ray crystal structure has been available to date, but spectroscopic and EXAFS measurements suggest[3] that the active site of Tyr is similar to that of Hc. The difference in biological function between the two proteins is that the protected buried active site in Hc is instead accessible to phenolic substrates in Tyr.[2a,3] The elegant biomimetic studies from a number of laboratories[1,2,5−8] have largely contributed to the understanding of the oxidized forms of Hc and Tyr.

Considerable progress has been made in the chemical modeling of Tyr-like monooxygenase activity.[1,5,6,9−18] Karlin et al. reported the first[10] model consisting of a binucleating ligand having a *m*-xylyl spacer between the two tridentate bis[2-

† Dedicated to Professor Richard H. Holm on the occasion of his 65th birthday.

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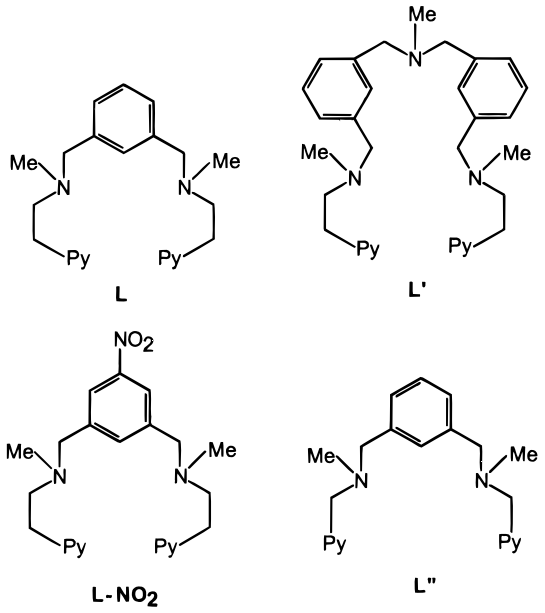
(2-pyridylethyl)amine] coordination units. Hydroxylation reactions have also been seen with other modified xylyl systems of Schiff bases.[13−17] Interestingly, these latter systems provide only two N-coodinations per copper. Martell and co-workers[18] demonstrated the first successful use of a xylyl-based macrocyclic ligand derived from diethylenetriamine to bring about aromatic ring hydroxylation.

Following the observations concerning (i) the stereochemistry of copper−nitrogen bonding in the crystal structures of Hc, (ii) the literature reports on Tyr models of xylyl-based Schiff base systems, and (iii) the fact that the active site of Tyr is more accessible to substrates, we initiated a program to systematically investigate Tyr-like activity using new *m*-xylyl-based ligand systems of the open-chain type[19a] or of the macrocyclic type,[19b] capable of providing only two N-coordinations to each copper site. Owing to the differing stereochemical preferences[20] of Cu^{II} (square pyramidal, trigonal bipyramidal, or intermediate between these two geometries) relative to Cu^{I} (tetrahedral or pyramidal) ready interconversions of these two oxidation states is expected to be facilitated by use of flexible ligands which can adjust their coordination geometry to the differing demands of the two oxidation states. To gain more insight into the reactivity of the binuclear Cu(I) complexes with dioxygen and in the dependency of the arene hydroxylation on ligand topology, we have undertaken the present investigation. In this paper we amplify our previous report[19a] by providing a detailed account of the synthesis and characterization of dicopper(I) complexes with L and L-NO_2 and their reactivity properties with molecular oxygen. The ligand L-NO_2 was synthesized to explore the possibility of stabilizing[11] a peroxo−dicopper(II) intermediate. We have also explored the effect of ligand chelate ring size L″ (Chart 1) on the reactivity of its dicopper(I) complex with O_2. Absorption spectroscopic and magnetic properties of the final dicopper(II) complexes have been investigated.

Chart 1



Experimental Section

Materials and Reagents. All reagents and solvents were obtained from commercial sources and used as received unless noted otherwise. Acetonitrile (CH_3CN) was dried by distillation over CaH_2. Further purification was achieved by $KMnO_4/Li_2CO_3$ treatment[21a] followed by distillation over P_4O_{10}. Chloroform and dichloromethane were made acid free by washing first with sodium bicarbonate solution and then thoroughly with water, followed by storing over anhydrous $CaCl_2$ for 24 h and distillation. A final distillation was done from calcium hydride. Tetrahydrofuran (THF) was distilled from calcium hydride. Ethanol and methanol were distilled from $Mg(OC_2H_5)_2$ and $Mg(OCH_3)_2$, respectively. Diethyl ether was dried first with anhydrous $CaCl_2$ and then refluxed with and distilled over sodium. Ethyl acetate was purified by refluxing over anhydrous K_2CO_3, followed by distillation. Tetra-*n*-butylammonium perchlorate (TBAP) was prepared/purified as before.[21] 1,3-Bis(bromomethyl)benzene and 1,3-bis(bromomethyl)-5-nitrobenzene were synthesized by following literature procedures.[22] All air-sensitive reactions were performed either in a Vacuum Atmospheres inert-atmosphere glovebox under a N_2 atmosphere (Department of Chemistry, University of Minnesota) or by using standard Schlenk and vacuum line techniques. Isolation and handling of dicopper(I) complexes were carried out inside the drybox. The salts $[Cu(CH_3CN)_4]X$ (X = ClO_4^- or SbF_6^-) were prepared as described in the literature.[23]

Ligand Synthesis. α,α′-Bis[*N*-methyl-*N*-(2-pyridylethyl)amino]-*m*-xylene (L). Method A.[19a] α,α′-*m*-Dibromoxylene (1.0 g, 3.74 mmol) and 2-(2-(methylamino)ethyl)pyridine (1.03 g, 7.6 mmol) were taken in CH_3CN (80 mL) along with solid Na_2CO_3 (1.5 g, 14.0 mmol). This mixture was refluxed for 4 days. To the resulting solution were added distilled water (30 mL) and CH_2Cl_2 (80 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, and kept overnight. Removal of solvent under reduced pressure afforded a brown oil. Yield: 1.3 g (92%). ^1H NMR (60 MHz; $CDCl_3$): δ 2.3 (6H, s, NMe), 2.93 (8H, s, NCH_2CH_2C), 3.56 (4H, s, $PhCH_2N$), 7.0−7.9 (10H, m, aromatic protons), 8.66−8.86 (2H, d, pyridine ring protons). Some minor peaks closely associated with the peaks for the methylene and methyl protons due to some other product(s) were also observed. All our ligand preparations gave similar results. Mass spectrum [*m*/*z* (relative intensity, assignment): 374 (7.4, M^+; corresponding to L), 240 (100) (the peak due to L′ was not observed due to instrument limitation)]. Positive-ion FAB mass spectrum (Figure S1, Supporting Information) [*m*/*z* (relative intensity, assignment): 375 {51, $(M + H)^+$; corresponding to HL^+},

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508 {9, $(M + H)^+$; corresponding to HL′$^+$}, 149 (100)]. On the basis of ^{1}H NMR spectral integration the % purity of L has been determined to be ∼90%. Positive-ion FAB mass peak intensities of L and L′ closely match with the ^{1}H NMR spectral result. Two well-separated peaks (a major and a minor) were detected in HPLC, and product ratios were determined to be closely similar to that obtained from ^{1}H NMR and positive-ion FAB mass spectra.

Method B. This methodology is adapted from the reported synthesis of a similar ligand by Gultneh et al.[24] α,α′-*m*-Dibromoxylene (0.5 g, 1.89 mmol) was dissolved in THF (10 mL), and to it a mixture of 2-(2-(methylamino)ethyl)pyridine (0.52 g, 3.82 mmol) and Et_3N (0.575 g, 5.69 mmol) in THF (10 mL) was added gradually with stirring. After 24 h of magnetic stirring at 298 K it was filtered and the light yellow colored liquid thus obtained was rotavaped to obtain a light brown oil (yield: 0.65 g, 92%). ^{1}H NMR (60 MHz; $CDCl_3$): δ 2.26 (6H, s, NMe), 2.9 (8H, s, NCH_2CH_2C), 3.56 (4H, s, $PhCH_2N$), 6.9−7.87 (10H, m, aromatic protons), 8.4−8.6 (2H, d, pyridine ring protons). The ^{1}H NMR spectrum (Figure S2, Supporting Information), mass spectrum [*m*/*z* (relative intensity, assignment): 374 (5.65, M^+), 240 (100)], and only one peak in HPLC confirmed its purity.

***p*-Nitro Derivative of L, L-NO$_2$.** The ligand L-NO_2 was prepared by the same procedure as that followed for the synthesis of L (method B).

A mixture of 2-(2-(methylamino)ethyl)pyridine (0.088 g, 0.647 mmol) and Et_3N (0.098 g, 0.97 mmol) in THF (2 mL) was added gradually with stirring to a solution of 1,3-bis(bromomethyl)-5-nitrobenzene (0.1 g, 0.324 mmol) in THF (2 mL). The resulting mixture was stirred at room temperature for 24 h. After filtration, the light yellow liquid thus obtained was rotavaped to obtain a yellow oil. Yield: 0.066 g (49%). ^{1}H NMR (60 MHz; $CDCl_3$): δ 2.23 (6H, s, NMe), 2.9 (8H, s, NCH_2CH_2C), 3.53 (4H, s, $PhCH_2N$), 6.90−7.97 (9H, m, aromatic protons), 8.37−8.57 (2H, d, pyridine ring protons).

α,α′-Bis[(*N*-methyl-*N*-(2-pyridylmethyl)amino]-*m*-xylene (L″). *m*-Xylylenediamine (0.252 g, 1.853 mmol) and 2-pyridinecarboxaldehyde (0.397 g, 3.71 mmol) were dissolved in C_2H_5OH (30 mL) and refluxed for 1 h. Solvent was then removed under reduced pressure, and the oil thus obtained was extracted with $CHCl_3$. Removal of solvent afforded the Schiff-base product as a semisolid. Yield: 0.57 g, ∼98%. ^{1}H NMR (60 MHz; $CDCl_3$): δ 4.80 (4H, s, $PhCH_2N$), 7.10−8.20 (10H, m, aromatic protons), 8.36−8.70 (4H, m, pyridine ring protons and −N═C−H protons). The Schiff base (0.60 g, 1.92 mmol) was then dissolved in CH_3OH (15 mL), and to it ∼6 equiv of $NaBH_4$ (0.44 g, 11.58 mmol) was added in portions. After each addition the reaction mixture was heated on a steam bath and subsequently cooled. This process was continued until there was no further effervescence. To the resulting mixture saturated brine solution (15 mL) was added, and this extracted 3−4 times with diethyl ether. The organic layer was collected and kept with anhydrous K_2CO_3, and finally solvent was removed to obtain a deep yellow oil. Yield: 0.58 g, ∼95%. ^{1}H NMR (60 MHz; $CDCl_3$): δ 2.20 (2H, s, −NH), 3.67−3.87 (8H, d, $PhCH_2N$ and NCH_2C), 7.00−7.67 (10H, m, aromatic protons), 8.40−8.60 (2H, d, pyridine ring protons). The amine thus obtained (0.58 g, 1.824 mmol) was mixed with formaldehyde (2.0−2.5 mL) and formic acid (2.5−3.0 mL), and the resulting mixture was refluxed at 90 °C for 24 h. It was then cooled in an ice bath, and a saturated solution of NaOH was added to it with stirring until the pH of the solution was 12. To the resulting mixture, $CHCl_3$ was added, and the organic layer was collected and dried over anhydrous Na_2SO_4. Finally the solvent was removed under reduced pressure to obtain the desired ligand L″ as a deep brown oil. Yield: 0.545 g, ∼ 86%. ^{1}H NMR (60 MHz; $CDCl_3$): δ 2.10 (6H, s, −NMe), 3.40−3.60 (8H, d, $PhCH_2N$ and NCH_2C), 6.83−7.73 (10H, m, aromatic protons), 8.33−8.50 (2H, d, pyridine ring protons). Mass spectrum [*m*/*z* (relative intensity, assignment): 346 (11.7, M^+), 255 (100)].

α,α′-Bis[*N*-methyl-*N*-(2-pyridylethyl)amino]-4-methylphenol (L′-OH).[25] A solution of 2,6-bis(chloromethyl)-4-methylphenol (1.48 g, 7.2 mmol)[25a] in ethyl acetate (20 mL) at 273 K was added to a solution of 2-[2-(methylamino)ethyl]pyridine (1.97 g, 14.4 mmol) and Et_3N (1.42 g, 14.4 mmol). This mixture was then stirred for 5 days at 298 K. After filtration, the solvent was removed and the residue was extracted with ethyl acetate (3 × 15 mL). Finally, the solvent was removed to obtain a deep brown oil. Yield: 2.75 g, ∼93%. ^{1}H NMR (60 MHz; $CDCl_3$): δ 2.10 (3H, s, ArMe), 2.23 (6H, s, NMe) 2.85 (8H, s, NCH_2CH_2), 3.56 (4H, s, $PhCH_2N$), 6.53−7.51 (8H, m, aromatic protons), 8.38 (2H, d, pyridine ring protons), ∼10.5 (1H, br, phenolic OH).

Syntheses of Complexes. Reaction of L (Method A) with Copper(I) and Subsequent Oxygenation. In dinitrogen-flushed CH_2Cl_2 (30 mL), solid $[Cu(CH_3CN)_4][ClO_4]$ (0.7 g, 2.14 mmol) was added and kept under magnetic stirring. The ligand L (0.402 g, 1.075 mmol) was dissolved in CH_2Cl_2 (30 mL) under a dinitrogen atmosphere and then added to the metal salt solution by a cannula. The mixture resulted in a yellow suspension of an extremely air-sensitive copper(I) complex. After stirring of the mixture for 3−4 h, it was exposed to dioxygen (1 atm; 298 K) and stirred for a further 12 h. A blue-gray compound precipitated along with a green solution. The blue-gray solid was collected by filtration, washed 3−4 times with CH_2Cl_2, and vacuum-dried. Yield: 0.45 g (47%, based on the composition $[Cu^{II}_2L(OH)(H_2O)][ClO_4]_3\cdot 2H_2O\cdot 0.5HCl$, **3a**). Solvent was removed from the green filtrate, and a CH_3CN solution of the solid thus obtained was left for slow evaporation. This afforded at first only a few blue crystals ($[Cu^{II}_2L'(OH)_2][ClO_4]_2$, **2b**) and a bulk of microcrystalline green compound. Yield: 0.32 g (40%, based on the composition $[Cu^{II}_2$(L-O)(OH)$][ClO_4]_2$, **2a**).

Characterization of Dicopper(II) Complexes. Green Crystals. Anal. Calcd for $[Cu^{II}_2$(L-O)(OH)$][ClO_4]_2$ (**2a**), $C_{24}H_{30}N_4Cl_2O_{10}Cu_2$: C, 39.35; H, 4.13; N, 7.65. Found: C, 39.57; H, 4.20; N, 7.82. IR (KBr, cm^{-1}, selected peaks): 3450 (m, ν(OH)), 1320 (s, ν(OPh)), 1100 and 620 (s, $\nu(ClO_4^-)$).Conductivity (CH_3CN, 10^{-3} M solution at 298 K): $\Lambda_M = 280\ \Omega^{-1}\ cm^2\ mol^{-1}$. Absorption spectrum [$\lambda_{max}$, nm ($\epsilon$, $M^{-1}\ cm^{-1}$)]: in CH_3CN, 620 (170), 352 (2220), 261 (7200), 241 (7400). The first two absorptions were recorded at a concentration of 0.68 mM, and the two highest energy peaks were recorded at a concentration of 0.27 mM. When the concentration was 3 mM the peak at 352 nm shifted to 392 nm ($\epsilon = 940\ M^{-1}\ cm^{-1}$).

Blue Crystals. Anal. Calcd for $[Cu^{II}_2L'(OH)_2][ClO_4]_2$ (**2b**), $C_{33}H_{43}N_5Cl_2O_{10}Cu_2$: C, 45.68; H, 4.99; N, 8.07. Found: C, 45.52; H, 4.80; N, 7.88. IR (KBr, cm^{-1}, selected peaks): 3600 (s, ν(OH)), 1100 and 620 (s, $\nu(ClO_4^-)$). Conductivity (CH_3CN, 10^{-3} M solution at 298 K): $\Lambda_M = 238\ \Omega^{-1}\ cm^2\ mol^{-1}$. Absorption spectrum [$\lambda_{max}$, nm ($\epsilon$, $M^{-1}\ cm^{-1}$)]: in CH_3CN, 589 (70), 361 (985), 264 (6240). The first two absorptions were recorded at a concentration of 2.51 mM, and the highest energy peak was at a concentration of 0.53 mM.

Blue-Gray Solid. Anal. Calcd for $[Cu^{II}_2L(OH)(H_2O)][ClO_4]_3\cdot 2H_2O\cdot 0.5HCl$ (**3a**), $C_{24}H_{37.5}N_4Cl_{3.5}O_{16}Cu_2$: C, 32.40; H, 4.22; N, 6.30. Found: C, 32.48; H, 4.15; N, 5.96. IR (KBr, cm^{-1}, selected peaks): 3530 (m, ν(OH)), 1100 and 620 (s, $\nu(ClO_4^-)$). Conductivity (CH_3CN, 10^{-3} M solution at 298 K): $\Lambda_M = 285\ \Omega^{-1}\ cm^2\ mol^{-1}$. Absorption spectrum [$\lambda_{max}$, nm ($\epsilon$, $M^{-1}\ cm^{-1}$)]: 1.01 mM in CH_3CN, 620 (120), 355 sh (895), 260 (5390).

Organic Product Identification. To check whether hydroxylation at the ligand site has taken place, copper was removed from the blue-gray solid as well as from the green compound by ammonia treatment.[10a] A detailed procedure for **2a** is described below. The organic extracts thus obtained were identified by ^{1}H NMR and/or positive-ion FAB mass spectral studies.

A 100 mg amount of green compound **2a** was dissolved in CH_2Cl_2 (40 mL), and to it liquor ammonia was added dropwise till the deep blue aqueous layer separated out. The organic layer was collected, washed 3−4 times with water, and finally dried over Na_2SO_4, and the solvent was removed under reduced pressure to get an oily yellow-brown product. The organic extract from the green compound showed the following characteristics in its ^{1}H NMR spectrum (60 MHz, $CDCl_3$): 2.23 (6H, s, NMe), 2.87 (8H, s, NCH_2CH_2C), 3.60 (4H, s, $PhCH_2N$), 6.83−7.67 (9H, m, aromatic protons), and 8.50−8.30 (2H, d, pyridine ring protons). Identification was confirmed by its positive-ion FAB mass spectrum (Figure S3, Supporting Information) [*m*/*z*

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(relative intensity, assignment): 391 {50, $(M + H)^+$; corresponding to $H(L\text{-}OH)^+$}, 149 (100)]. A violet coloration was obtained when freshly prepared $FeCl_3$ solution was added to an ethanolic solution of the organic extract obtained from the green solid **2a**, confirming the presence of the phenolic-OH group in the organic product. Additionally, the ^1H NMR spectrum of L′-OH (L-OH with a methyl group at 4-position of the aromatic ring) is closely similar to that obtained for L-OH. Similar ammonia treatment on the blue-gray solid **3a** gave only unchanged ligand L.

Isolation of Copper(I) Complexes with L (Synthesized by Method B). $[Cu_2L(CH_3CN)_2]X_2$ (X = ClO_4^-, 1a, or SbF_6^-, 1b). To a stirred solution of L (0.10 g, 0.267 mmol) in CH_2Cl_2 (2 mL) was added solid $[Cu(CH_3CN)_4]X$ (X = ClO_4^- or SbF_6^-) (0.53 mmol). After being stirred for 10 min, the starting suspension slowly dissolved to generate a homogeneous yellow solution, at which time diethyl ether (∼5 mL) was added with vigorous stirring. This procedure resulted in the separation of a yellow solid, which was washed several times with diethyl ether, and dried under vacuum to yield a light yellow powder (for ClO_4^- salt, 0.21 g, 91%; for SbF_6^- salt, 0.27 g, 90%). ^1H NMR of **1b** (CD_3CN, 300 MHz): δ 2.40 (6H, s, NMe), 2.75 (4H, s, NCH_2CH_2), 2.99 (4H, s, NCH_2CH_2), 3.84 (4H, s, $PhCH_2$), 7.33 (7H, s, aromatic protons), 7.39 (1H, s, aromatic proton), 7.79 (2H, t, $J = 7.5$ Hz, aromatic protons), and 8.43 (2H, s, pyridine protons). ^1H NMR of **1b** (CD_2Cl_2, 500 MHz): δ 2.27 (6H, s, CH_3 of coordinated CH_3CN), 2.68 (6H, s, NMe), 2.90 (4H, s, NCH_2CH_2), 3.02 (4H, s, NCH_2CH_2), 3.85 (4H, s, $PhCH_2$), 7.33−7.48 (m, 7H aromatic protons), 7.64 (1H, s, aromatic proton), 7.82 (2H, t, $J = 8.0$ Hz, aromatic protons), and 8.33 (2H, s, pyridine protons). FT IR (KBr, cm^{-1}): for SbF_6^- salt, 2280 (C≡N), 658 (SbF_6^-); for ClO_4^- salt, 2281 (C≡N), 1093 (ClO_4^-).

$[Cu_2(L\text{-}NO_2)(CH_3CN)_2][SbF_6]_2$ (1c). The synthesis of this compound was carried out following a similar methodology as described above. Yield: ∼ 90%. ^1H NMR (CD_2Cl_2, 300 MHz): δ 2.26 (6H, s, NMe), 2.69 (6H, s, CH_3 of coordinated CH_3CN), 2.94 (4H, s, NCH_2CH_2), 3.05 (4H, s, NCH_2CH_2), 3.98 (4H, s, $PhCH_2$), 7.32−7.36 (m, 4H aromatic protons), 7.84 (2H, s, aromatic protons), 8.01 (1H, t, $J = 8.0$ Hz, aromatic proton), and 8.33 (2H, s, pyridine protons).

Reaction of Pure L with Copper(I) and Subsequent Oxygenation. The reactions were carried out in four different solvents (CH_2Cl_2, CH_3OH, CH_3CN, and DMF) by using the same amount of ligand and copper(I) salt $[Cu(CH_3CN)_4][ClO_4]$ and by following a similar procedure. A representative case is described below.

In CH_2Cl_2. To dinitrogen-flushed CH_2Cl_2 (8 mL) solid $[Cu(CH_3CN)_4][ClO_4]$ (0.175 g, 0.536 mmol) was added and kept under magnetic stirring. To it the ligand L (0.100 g, 0.267 mmol) dissolved in deoxygenated CH_2Cl_2 (8 mL) was added dropwise by a cannula. The resulting yellow suspension of an extremely air-sensitive dicopper(I) complex was stirred for 3−4 h under a dinitrogen atmosphere and finally exposed to dioxygen (1 atm; 298 K) and allowed to stir. After ∼12 h, a blue-gray solid precipitated out from a green solution. The blue-gray solid **3a** was collected by filtration, washed thoroughly with CH_2Cl_2, and finally vacuum-dried. Yield: 0.12 g (50%). Solvent was removed from the green filtrate, and the solid thus obtained was dissolved in CH_3CN and left for slow evaporation. This yielded the bulk of the microcrystalline green compound **2a**. Yield: 0.06 g (30%). The yields of green solid in various solvents are as follows: CH_3OH, 0.150 g (75%); CH_3CN, 0.175 g (90%); DMF, 0.175 g (90%).

Reaction of L″ with Copper(I) and Subsequent Oxygenation. Solid $[Cu(CH_3CN)_4][ClO_4]$ (0.095 g, 0.291 mmol) was dissolved in degassed CH_2Cl_2 (8 mL), and the Schlenk flask was kept immersed in a CH_3OH−slush bath at −60 °C. To this the ligand L″ (0.050 g, 0.145 mmol) dissolved in CH_2Cl_2 (8 mL) was added and stirred under a dinitrogen atmosphere. The mixture, a yellow suspension of supposedly dicopper(I) complex, was then exposed to dioxygen at −60 °C and then gradually the flask was warmed to 298 K. This procedure was adopted to avoid the formation of a "brown solution" which otherwise was taking place when the oxygenation reaction was carried out at room temperature (this solution did not afford any tractable solid). The color of the suspension changed gradually from yellow to brown to finally green. After stirring of the reaction mixture at 298 K for 4−5 h, the color of the precipitate changed to light blue with a brown supernatant. The precipitate was filtered off, washed thoroughly with CH_2Cl_2, and finally vacuum-dried to isolate a light blue solid. Yield: 0.09 g (75%, based on the composition $Cu^{II}_2L''(OH)(ClO_4)_3(H_2O)_2$, **3b**). Anal. Calcd for $C_{22}H_{31}N_4Cl_3O_{15}Cu_2$: C, 32.03; H, 3.79; N, 6.79. Found: C, 32.31; H, 3.86; N, 6.65. IR (KBr, cm^{-1}, selected peaks): 3420 (m, ν(OH)), 1140, 1100, 1080, 630, and 620 (s, $\nu(ClO_4^-)$). Conductivity (CH_3CN, 10^{-3} M solution at 298 K): $\Lambda_M = 260\ \Omega^{-1}\ cm^2\ mol^{-1}$. Absorption spectrum [$\lambda_{max}$, nm ($\epsilon$, $M^{-1}\ cm^{-1}$)]: 0.98 mM in CH_3CN, 625 (185), 290 (sh) (5070), 259 (12 500).

Caution! *Perchlorate salts of compounds containing organic ligands are potentially explosive*!

Measurements. Elemental analyses were obtained from either the Indian Association for the Cultivation of Science, Calcutta, India, or National Chemical Laboratory (NCL), Pune, India. IR spectra were recorded as KBr pellets with the help of a Perkin-Elmer 1320 or on a Mattson Polaris FTIR spectrophotometers. Electronic spectra were measured with a Perkin-Elmer Lambda 2 spectrophotometer, and solid-state electronic spectra (reflectance spectra) were measured using paraffin oil. Low-temperature UV−vis spectra were recorded (Department of Chemistry, University of Minnesota) on a Hewlett-Packard HP8452A diode array spectrophotometer (190−820 nm scan range) by using a custom manufactured vacuum dewar equipped with quartz windows. Low temperatures were achieved by adding liquid nitrogen to a CH_3OH bath. The bath temperature was monitored by using a resistance thermocouple probe (Fluke 51 K/J thermometer). ^1H NMR spectra were obtained on a PMX-60 JEOL (60 MHz) instrument or Brüker WP-80 (80 MHz) or VXR-500 (500 MHz) NMR spectrometers using $CDCl_3$, CD_2Cl_2, or CD_3CN solutions. Chemical shifts (in ppm) are referenced to the residual solvent peak(s) or TMS. HPLC experiments were performed on a Pharmacia LKB model 2248, using a reverse-phase C_{18} column at a flow rate of 1 mL/min. Elution was achieved by 40:60 (v/v) CH_3CN/CH_3OH, and its profile was monitored by Pharmacia LKB model 2141 at 367 nm. Solution electrical conductivity measurements were made with an Elico (Hyderabad, India) Type CM 82 T conductivity bridge. Solution magnetic susceptibility measurements were made by the usual NMR method[26] with a PMX-60 JEOL (60 MHz) spectrometer and made use of the paramagnetic shift of the methyl protons of CH_3CN or TMS reference as the measured NMR parameter. Diamagnetic corrections[27] were taken from literature tabulations. Mass spectra were obtained with a Finnigan MAT-1020-B 70-eV mass spectrometer at the NCL, Pune, India. Positive-ion fast atom bombardment (FAB) mass spectra were recorded at the Central Drug Research Institute, Lucknow, India, on a JEOL SX 102/DA-6000 mass spectrometer/data system using argon gas ionization in a matrix of *m*-nitrobenzyl alcohol as the matrix and CH_3CN as solvent.

Variable-temperature magnetic susceptibility measurements were obtained on polycrystalline samples (powdered form) by the Faraday method using a locally built susceptometer. The system consists of an electromagnet (Polytronic Corporation, Mumbai, India), a microbalance (Sartorius, Göttingen, Germany), and a closed-cycle cryostat (CTI cryogenics). The calibration of the system and the details of measurements are already reported in the literature.[28] Effective magnetic moments were calculated from $\mu_{eff} = 2.828[\chi_M T]^{1/2}$, where χ_M is the corrected molar susceptibility. The diamagnetic contributions were $-368 \times 10^{-6}\ cm^3\ mol^{-1}$ for **2a**, $-473 \times 10^{-6}\ cm^3\ mol^{-1}$ for **2b**, $-445 \times 10^{-6}\ cm^3\ mol^{-1}$ for **3a**, and $-402 \times 10^{-6}\ cm^3\ mol^{-1}$ for **3b**. The data were fitted to the Bleany−Bowers expression (eq 1) for two

$$\chi_M = 2N\beta^2g^2/3kT[1 + {}^1/_3\exp(-2J/kT)]^{-1}(1-\rho) + N\beta^2g^2\rho/2kT + 2N_\alpha \quad (1)$$

interacting $S = {}^1/_2$ centers developed under the usual isotropic (Heisenberg) exchange Hamiltonian $H = -2JS_1 \cdot S_2$.[27] Inclusion of terms for the temperature-independent paramagnetic susceptibility (TIP) and for possible sample contamination of monomeric copper(II) impurity exhibiting Curie behavior yielded the appropriate equation (eq 1). In

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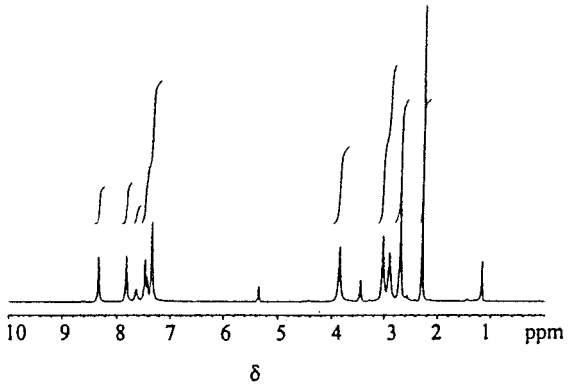

Figure 1. ^{1}H NMR spectrum of $[Cu_2L(CH_3CN)_2][SbF_6]_2$ (**1b**) in CD_2Cl_2.

this expression, N, g, and k have their usual meaning, ρ is the fraction of monomeric impurity, and N_α is the temperature-independent paramagnetism; $2J$ is the energy differnce between the singlet and triplet states, and χ_M is the molar susceptibilty per dimer. A nonlinear regression analysis was carried out with J, g, and ρ as floating parameters.

X-band EPR spectra were recorded with a Varian E-109 C spectrometer fitted with a quartz dewar for measurements at liquid dinitrogen temperature. The spectra were calibrated with the help of DPPH ($g = 2.0037$).

Results and Discussion

Syntheses of Ligands and Dicopper(I) Complexes. The dinucleating ligands (Chart 1) were prepared by standard methods (Experimental Section). To minimize the complications in handling with an impure ligand L (method A),[19a] in the meantime we successfully developed a methodology (method B) for the synthesis of pure ligand L. Isolation of the dicopper(I) complexes were achieved by the addition of 2 equiv of $[Cu(CH_3CN)_4]X$ ($X = ClO_4^-$ or SbF_6^-) to the solution of appropriate pure ligand in CH_2Cl_2. The composition/purity of the dicopper(I) complexes were judged by ^{1}H NMR spectroscopy for $[Cu_2L(CH_3CN)_2]X_2$ ($X = ClO_4^-$ (**1a**), SbF_6^- (**1b**)) and $[Cu_2(L\text{-}NO_2)(CH_3CN)_2][SbF_6]_2$ (**1c**). Additional proof of their compositions were obtained from FT IR (**1a**,**b**). The ^{1}H NMR spectra of **1b**,**c** are displayed in Figure 1 and Figure S4, Supporting Information, respectively.

Reactivity of $[Cu_2L(CH_3CN)_2]X_2$ ($X = ClO_4^-$ (1a), SbF_6^- (1b)) and $[Cu_2(L\text{-}NO_2)(CH_3CN)_2][SbF_6]_2$ (1c) with Dioxygen at −80 °C. It has been proposed[1,3,5,6,9−18] that for regiospecific aromatic ring hydroxylation by copper with *m*-xylyl-based ligand systems, the reaction proceeds through the formation of a (μ-η^2:η^2-peroxo)dicopper(II) intermediate which has an intense purple/orange-red color depending on the nature of the ligand system. This peroxo species is unstable at higher temperatures but fairly stable for most of the systems at low temperatures, ∼−80 °C.[11,12] Kitajima et al.[29] determined the structure of this novel dicopper−dioxygen adduct with their tris(3,5-diisopropylpyrazolyl)borate ligand.

To investigate possible formation of the peroxo species, with the present ligand L, CH_2Cl_2 and THF solutions of the dicopper(I) complexes were exposed to molecular oxygen at −80 °C and absorption spectral behavior was investigated at this temperature. In both solvents the solution turned green within the time of exposure and an absorption band appeared at 352 nm ($\epsilon \sim 2000$ M^{-1} cm^{-1}), which did not change on warming the solution to room temperature (Figure 2). It is thus clear that the peak at 352 nm is not due to peroxo → Cu(II) charge-transfer[11,12] but due to PhO^-/OH^- → Cu(II) charge-transfer transition, originating due to the formation of the phenoxo- and hydroxo-bridged dicopper(II) complex (vide infra). As here the oxygenation reactions are instantaneous, we have not been able to determine the reaction stoichiometry of Cu^I_2/O_2 at room temperature from the measurements of the uptake of dioxygen (manometry). The dicopper(I) complexes **1a**,**b** grossly resemble Karlin's system with the primary difference that Karlin's ligand provided two ethylpyridine arms from each aliphatic nitrogen and only one such arm is present in our ligand.

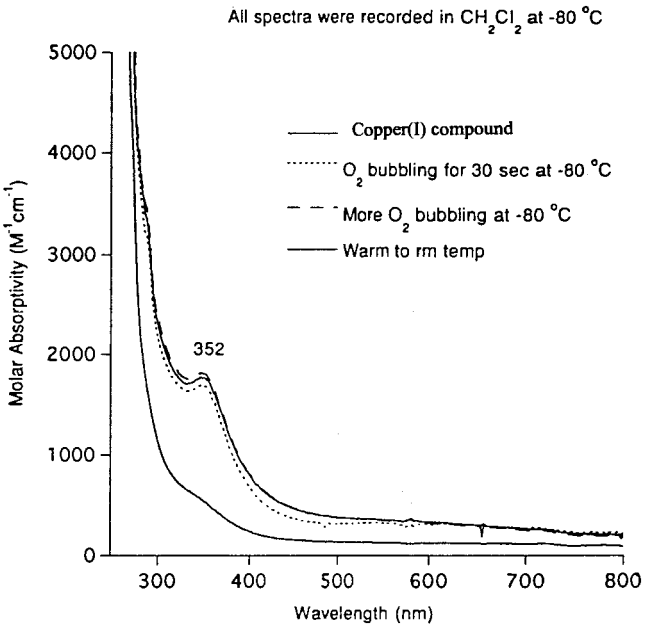

Figure 2. Oxygenation reaction of $[Cu_2L(CH_3CN)_2][SbF_6]_2$ (**1b**) in CH_2Cl_2 at − 80 °C. The lower trace (solid line) is for the dicopper(I) compound.

Using a *p*-nitro derivative of the parent ligand, Karlin et al.[11] spectroscopically identified the peroxo species which was fairly stable at −80 °C. The presence of an electron-withdrawing $-NO_2$ substituent in the *para*-position made the xylyl ring electron poor and hence decreased the rate of subsequent electrophilic attack of the peroxo species to the aromatic ring. Hoping along the same line, we synthesized the *p*-nitro derivative of L, L-NO_2, and its dicopper(I) complex. However, when this complex **1c** dissolved in either CH_2Cl_2 or THF was exposed to O_2 at −80 °C, we could not detect any peroxo intermediate. The otherwise kinetically favorable hydroxylation of the aromatic ring was observed. In essence, it implies that the peroxo intermediate is of insufficient stability to be observed because of the low barrier for its subsequent reaction.

Both Karlin's complexes and these ones oxygenate quickly at low temperature. To extract information regarding relative stabilization of Cu^{II} over Cu^I oxidation state (electronic effect), in a given solvent, we investigated briefly the redox behavior of the dicopper(I) complex of L and compared it with that of Karlin's system. When examined by cyclic voltammetry under anaerobic conditions, complex **1a** (generated in DMF) exhibits a single oxidative redox process with peak-to-peak separation of 240 mV, for the redox couple $[Cu^{II}_2L(CH_3CN)_2]^{4+}/[Cu^I_2L(CH_3CN)_2]^{2+}$ at $E_{1/2} = -0.26$ V vs SCE. A typical CV scan is displayed in Figure 3. The $E_{1/2}$ value for the Karlin's system is reported to be 0.31 V vs Ag/AgCl,[30] i.e., 0.29 V vs

(29) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277 and references therein.

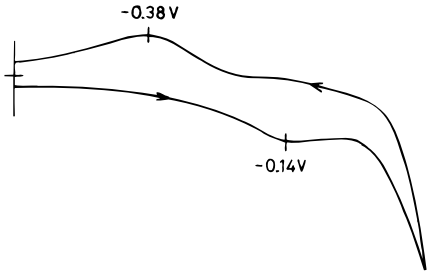

Figure 3. Cyclic voltammogram of solution-generated $[Cu_2L(DMF)_2][ClO_4]_2$ in DMF at a platinum working electrode ($\upsilon = 50$ mV s^{-1}).

SCE. Most interestingly, the $E_{1/2}$ value for our system is 550 mV more cathodic than that of Karlin's system. The CV result convincingly justifies the observed enhanced oxygen sensitivity of our dicopper(I) complexes. It should be emphasized here that although the reduction potential is a good predictor of the reactivity of the copper(I) complex toward dioxygen, it is not directly correlated with the feasibility for the formation of the dioxygen adduct, since the redox potentials are defined for outer-sphere-type electron-transfer reactions.[1a]

Reaction between L (Prepared by Method A) and $[Cu(CH_3CN)_4][ClO_4]$ and Subsequent Oxygenation in CH_2Cl_2 at Room Temperature. In the initial stages of this work, synthesis of L was achieved by method A. From ^{1}H NMR and positive-ion FAB mass spectra it was revealed that it contains some minor impurity. This impurity was eventually identified[19a] from the X-ray structure of the isolated dicopper(II) complex (**2b**).

Initial synthetic reactions of L with $[Cu(CH_3CN)_4][ClO_4]$ [0.4 g of L and 0.7 g of the copper(I) salt (Cu:L = 2:1)] were carried out in CH_2Cl_2 (~30 mL) under a dinitrogen atmosphere. The yellow solution with a yellow suspension[19a] thus obtained was exposed to dioxygen. After 12 h, the reaction mixture turned dark green and afforded green phenoxo- and hydroxo-bridged dicopper(II) complex (**2a**) as the major isolated solution product with a very small amount of light blue dihydroxo-bridged dicopper(II) complex **2b**.

Interestingly, an appreciable amount of CH_2Cl_2-insoluble blue-gray compound, supposedly irreversible oxidation product, was also isolated.[19a]

Reactivity of Solution-Generated $[Cu_2L(CH_3CN)_2][ClO_4]_2$ (1a) with Dioxygen at Room Temperature. (a) In CH_2Cl_2. Following a similar reaction sequence as stated in the previous section, we isolated only two dicopper(II) compounds: green microcrystalline (**2a**) and blue-gray (**3a**).[31]

(b) In CH_3CN, DMF, and CH_3OH. In these solvents the reactions were carried out under identical conditions as that in CH_2Cl_2. In these cases, on exposure to dioxygen, initially formed yellow solution gradually changed to dark green, which eventually allowed the isolation of the green microcrystalline solid **2a**. Interestingly, in these solvents no blue-gray solid was formed.

(c) Effect of Solvent on the Aromatic Ring Hydroxylation. The role of solvent is expected to be of significance, since the availability of the open coordination site is depended on the coordinating ability of the solvents.[1a] Moreover, the stability of the dioxygen adduct is expected to be influenced by the interaction between the dioxygen adduct and the solvent. However, it is to be noted that the actual coordination number at Cu(I) centers in the present investigation is unsure, given the solvent coordination from $Cu(CH_3CN)_4^+$.

From the results presented in the previous section, we infer that the extent of aromatic ring hydroxylation with our binucleating ligand L is very much dependent on the nature of the medium in which the oxygenation reaction has been performed. The formation of the phenoxo- and hydroxo-bridged dicopper(II) complex **2a**, which is the aromatic ring hydroxylation product, varies with the polarity of the solvent. In polar solvents[32] like CH_3CN (dielectric constant, $\epsilon = 37.5$) and DMF ($\epsilon = 36.7$), the extent of hydroxylation was almost quantitative, which decreased in a comparatively less polar CH_3OH ($\epsilon = 32.6$) and was considerably less in a nonpolar solvent like CH_2Cl_2 ($\epsilon = 9.1$).

Reaction between L″ and $[Cu(CH_3CN)_4][ClO_4]$ and Subsequent Oxygenation in CH_2Cl_2. The ligand L″ was synthesized to specifically pinpoint the effect of ligand topology, to bring about aromatic ring hydroxylation with our parent *m*-xylyl-based binucleating ligand L. It is to be noted that on coordination while L gives rise to six-membered chelate ring, L″ provides five-membered chelate ring. Treatment of L″ with 2 equiv of $[Cu(CH_3CN)_4][ClO_4]$ in CH_2Cl_2 under dinitrogen at −60 °C, followed by exposure to dioxygen and slowly warming up the reaction mixture to 298 K, resulted in an immediate color change of the suspension from yellow to light blue. We confirmed that hydroxylation of the benzene ring of the ligand had not occurred, by isolating the ligand from the isolated dicopper(II) complex **3b** (vide infra). The organic extract has the same ^{1}H NMR spectral feature as that in L″.

Identification of the Copper(II) Products: Green 2a, Blue 2b, Blue-Gray 3a, and Light Blue 3b. IR spectra of **2a**,**b** display absorptions due to ν(O−H) and $\nu(ClO_4^-)$. The complex **2a** displays an additional phenolate ν(C−O) absorption.[19b] Elemental analyses, IR, and solution electrical conductivity data[33] of the dicopper(II) complexes are in agreement with the following formulations: $[Cu_2(L-O)(OH)][ClO_4]_2$, **2a**; $[Cu_2L'(OH)_2][ClO_4]_2$, **2b**. Complex **3a**, which is an "irreversibly oxidized product",[11,12,34−38] displays IR absorption due to water and/or hydroxo coordination.[39] Interestingly, for **3b** split absorptions due to bridging ClO_4^- coordination are clearly observable.[40] On the basis of elemental analysis, solution electrical conductivity data (1:2 electrolyte),[41] and additional solution behavior,[42] we propose the unhydroxylated product **3a** to have the composition $[Cu_2L(OH)(H_2O)][ClO_4]_3 \cdot 2H_2O \cdot 0.5HCl$. Final

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(41) Complex **3a** is expected to behave as 1:3 electrolyte, not the observed 1:2 electrolytic behavior.[33] It is proposed to be due to their rearrangements in CH_3CN solution: **3a** to the doubly hydroxy-bridged complex, $[Cu_2L(OH)_2][ClO_4]_2 \cdot 2H_2O$.

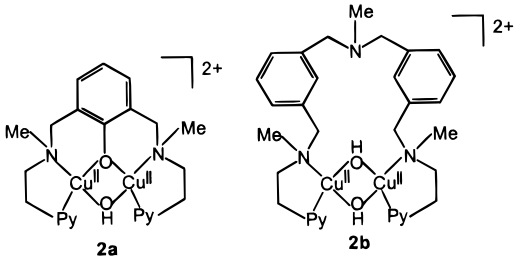


Figure 4. Schematic representations of the structures of the dicationic parts of $[Cu_2(L\text{-}O)(OH)][ClO_4]_2$ (**2a**) and $[Cu_2L'(OH)_2][ClO_4]_2$ (**2b**).

Table 1. X-ray Structural Metric Parameters[19a] and 2*J* Values for **2a**,**b**

	2a	**2b**
Cu···Cu (Å)	2.999 (1)	3.004 (2)
torsion angle of the Cu_2O_2 unit (deg)	∼7	∼12
average angles between the planes N−Cu−N and O−Cu−O (deg)	∼6	∼2
$2J$ (cm^{-1})	−440	−258

proof of the presence of a hydroxo bridge and an aquo bridge came from its temperature-dependent magnetic susceptibility measurements and spectral titration experiments (vide infra).

It is worth mentioning here that Karlin et al.[11] proposed a single hydroxo-bridged tricationic species, similar to **3a**, for their irreversibly oxidized product. In the positive-ion FAB mass spectra of **3a**,**b**, intense peaks were observed at *m*/*z* values of 537 and 509, respectively, corresponding to the presence of species $\{H[Cu^{II}_2L(OH)(H_2O)]\}^{4+}$/$\{[Cu^{II}_2L(H_2O)_2]\}^{4+}$ and $\{[Cu^{II}_2L''(H_2O)_2]^{4+}\}$, respectively (Figure S5, Supporting Information). Unfortunately, all the attempts to grow crystals of **3a**,**b** suitable for X-ray analysis and thus fully characterize these complexes in the solid state have been unsuccessful so far. Even we could not obtain elemental analysis data better than that reported here.

Description of the Structures. (a) $[Cu_2(L-O)(OH)][ClO_4]_2$ (2a). A schematic view of the cationic part of **2a** and metric parameters pertinent to this work are in Figure 4 and Table 1, respectively. The X-ray structure of **2a**[19a] underscores the incorporation of two O atoms into the complex: one into the aryl hydrogen bond and the other into the hydroxy bridge.

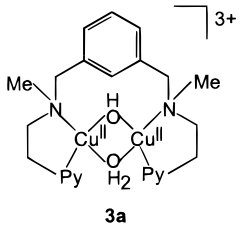
The average Cu−O (phenoxo: 1.961 Å; hydroxo, 1.913 Å), Cu−N (amine, 2.017 Å; pyridine, 2.003 Å), and Cu- - -Cu distances[19a] are closely similar to related complexes.[10,16,17] Considering the bond lengths and angles, it reveals that the geometry around each copper(II) ion in **2a** is distorted square planar. The Cu atoms lie more or less in the plane containing the O and the N atoms [one Cu atom being ∼0.04 Å and the other atom being ∼0.02 Å out of plane]. The two Cu(II) ions are in almost identical coordination environments.

(b) $[Cu_2L'(OH)_2][ClO_4]_2$ (2b). Figure 4 depicts a schematic view[19a] of the cationic part of **2b**, and pertinent bonding parameters are given in Table 1. The trend in the Cu−N (amine, 2.045 Å; pyridine, 1.997 Å) and Cu−O (1.925 Å) bonding parameters is closely similar to that observed in **2a**. The average Cu−O bond length and Cu−O−Cu angle are typical of the presence of dihydroxy bridges.[44−46] Most interestingly, the Cu_2O_2 unit is bent (hinge distortion). The copper atom is almost in the coordination plane (out of plane displacement is only 0.02 Å).

Visible Absorption Spectra of the Copper(II) Complexes: Green (2a), Blue (2b), Blue-Gray (3a), and Light Blue (3b). The electronic spectrum of **2a** (Figure S6, Supporting Information) shows a ligand field band at 620 nm. A ∼3 mM solution of **2a** gives an intense peak at 392 nm which shifts on dilution (∼0.7 mM) to 352 nm. The exact cause of this behavior is not very clear. The high-energy transition is due to $PhO^- \rightarrow$ Cu(II) and/or $OH^- \rightarrow$ Cu(II) ligand-to-metal charge-transfer (LMCT) origin.[10−13,15−18] The absorption spectrum of a ∼2.5 mM solution of **2b** (Figure S6, Supporting Information) displays a ligand field band at 589 nm and an intense peak at 361 nm, typical of an $OH^- \rightarrow$ Cu(II) charge-transfer band.[15,38] Intraligand charge-transfer bands were also observed for both the complexes.

The bluish gray irreversible oxidation product **3a** instantaneously changes in CH_3CN to generate a bluish green solution, implying a structural change. This was also clear from the difference in its spectral behavior in the solid state and in solution. The solid-state reflectance spectrum (in paraffin oil) exhibits a broad band at ∼560 nm, and when the sample was diluted, only two shoulders at 365 and 277 nm were observed. In contrast, a ∼1 mM CH_3CN solution displays a ligand field band at 620 nm, a weak shoulder at 355 nm, and a peak at 260 nm of intraligand origin. It is interesting to note here that the position of the band at 355 nm varies with concentration. Moreover, the shoulder is not observable in very dry CH_3CN; however, on dilution this shoulder becomes prominent, probably due to attainment of additional hydroxo-bridging (vide infra). The band at ∼355 nm is supposedly due to $OH^- \rightarrow$ Cu(II) charge transfer.[15,38] The behavior in not so dry CH_3CN is thus understandable. Interestingly, no color change is observed when **3b** is dissolved in CH_3CN. The spectral behavior of **3b** (d−d transition at 625 nm and a shoulder of charge-transfer origin at 290 nm) suggests that each copper(II) center is four-coordinate[47] with no hydroxo bridging as in **3a**.

To look into the nature of proposed bridging group(s) (aquo/hydroxo) in **3a**, the following controlled experiments were



performed. It has been observed that addition of 1 equiv of $HClO_4$ (in CH_3CN) the band at ∼ 355 nm disappears. Ad-

(42) We were rather surprised to detect chloride ion, as the AgCl precipitate, from the hot aqueous nitric acid solution of **3a**. Additionally, we could detect the presence of Cl^- ion as trapped HCl from the acidic nature of suspended aqueous solution of this complex (gravimetric analysis of chloride as AgCl: calcd, 2.00; found, 1.98). Dichloromethane must be the likely source of the chloride ion. It should be mentioned here that Karlin et al.[43] and Sorrell et al.[15] also found that their copper(I) complexes react with CH_2Cl_2 resulting in the formation of chlorocopper(II) compounds.

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ditionally, it causes a red shift of the d−d band. However, on addition of 4 equiv of an aqueous solution (40%) of TBA^+OH^- in CH_3CN the band reappears (Figure S7, Supporting Information). This demonstrates the presence of a hydroxo group in **3a**, which rearranges to dihydroxo species in solution (vide infra). For **3b**, we have noticed that addition of 1 equiv of the above base causes decomposition of the complex and addition of 2 equiv of acid generates a weak shoulder at ∼340 nm. With the results at hand we are not in a position to propose the structure of **3b**.

Magnetism of Copper(II) Complexes. (a) Solid-State Behavior. The structurally chatracterized complexes **2a**,**b** have given us an unique opportunity to study the magnetic behavior of two dicopper(II) complexes with phenoxo-/hydroxo- and bis(hydroxo)-bridging having closely similar terminal ligation. Therefore, there is a possibility to arrive at a magneto−structural trend. The detailed temperature-dependent magnetic studies of **2a**,**b**, and **3a**,**b** in the solid state (Faraday method) were undertaken to elucidate the extent of magnetic exchange interactions in these systems.

For **2a**,**b** the measurements were carried out in the temperature range 25−300 K. In the case of **2a**, the value of μ_{eff}/Cu at 300 K is found to be 1.13 μ_B which decreased sharply to 0.35 μ_B at 100 K and 0.24 μ_B at 25 K. A plot of molar susceptibilty (per dimer) versus temperature is illustrated in Figure 5. The behavior is typical of a strongly antiferromagnetically coupled system. A sharp rise in χ_M at low temperatures indicates the presence of small amount of paramagnetic impurity. The best fit obtained using eq 1 (Figure 5) gave $2J = -440$ cm^{-1}, $g = 2.05$, and $\rho = 0.016$. The large negative value of J indicates a strong coupling between the two copper centers, expected for these types of systems.[48,49] In the related system of Karlin et al. even stronger coupling was observed ($2J = -600$ cm^{-1}).[48] For **2b**, the value of μ_{eff}/Cu at 300 K is 1.50 μ_B and it decreases to 0.72 μ_B at 100 K and finally to 0.43 μ_B at 25 K. This behavior is closely similar to that of **2a**. Figure 5 displays the plot of molar susceptibility (per dimer) versus temperature with the following values: $2J = -258$ cm^{-1}; $g = 2.13$; $\rho = 0.054$. The extent of magnetic coupling is comparable to closely related systems.[46] This result reveals that in **2b** the extent of coupling is much reduced than that in **2a**. The pronounced effect of the extent of magnetic coupling in going from **2a** (phenoxo/hydroxo-bridge) to **2b** (dihydroxo bridge) for a closely similar ligand environment is worth noticing.

For **3a**, the value of μ_{eff}/Cu is 1.86 μ_B at 300 K. In fact, the observed value is that expected for a mononuclear magnetically dilute copper(II) ion.[47] However, temperature-dependent magnetic susceptibility measurements revealed that the μ_{eff}/Cu value at 300 K gradually decreases to 1.43 μ_B at 81 K. A plot of molar susceptibilty (per dimer) versus temperature along with nonlinear least-squares fitting of the data using eq 1 is displayed in Figure 6. This plot yielded the following values: $2J = -70$ cm^{-1}; $g = 2.15$; $\rho = 0.030$. The temperature-dependent behavior of this complex is also that expected for an antiferromagnetically coupled system. It should be noted, however, that for **3a** the extent of magnetic coupling is much reduced. Comparing the magnetic behavior of **3a** with that of a structurally characterized dicopper(II) complex with an aquo bridge in addition to a hydroxy in a macrocyclic environment[39] gives confidence to our proposed structure. For **3b**, the value of μ_{eff}/Cu is 1.98 μ_B at 300 K and is gradually decreases to 1.77 μ_B at 81 K. A similar analysis gives rise to the following parameters: $2J = -4$ cm^{-1}; $g = 2.15$; $\rho = 0.00025$. Thus the extent of magnetic coupling follows the order **2a** > **2b** > **3a** > **3b**.

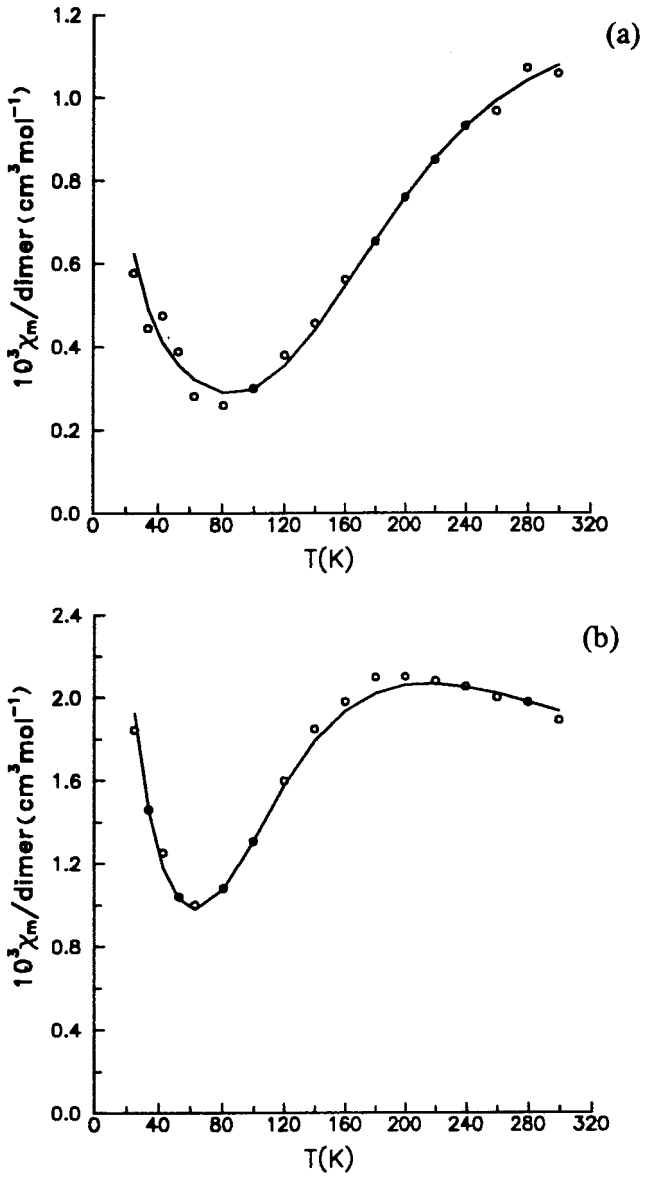

Figure 5. Plots of molar susceptibility (χ_M per dimer) versus temperature for polycrystalline samples of (a) $[Cu_2(L\text{-}O)(OH)][ClO_4]_2$ (**2a**) and (b) $[Cu_2L'(OH)_2][ClO_4]_2$ (**2b**). The solid lines result from a least-squares fit of the susceptibility data to eq 1. See the text for fitting parameters.

(b) Solution-State Behavior. The effective magnetic moments for **2a** and **3a**,**b** in CH_3CN solution (300 K) were determined by using the NMR method.[26] The μ_{eff}/Cu value for **2a** was found to be 1.05 μ_B, in conformity with the solid-state value. Most interestingly, the value of μ_{eff}/Cu for **3a** is 1.55 μ_B, which is considerably less than the solid-state value (1.86 μ_B). This could be due to the following reason. In CH_3CN solution the water molecule bridged to copper(II) centers reorganizes to provide an additional hydroxo bridge between the two copper(II) centers, $\{Cu_2L(OH)_2\}^{2+}$ (vide supra). This in turn provides a better pathway for magnetic coupling and thus results in lower value of μ_{eff}/Cu. In fact, the data decrease with time. After 24 h, the value becomes 1.41 μ_B. This proposition provides an explanation for its observed conductivity data (1:2 electrolytic behavior). Due to difficulty in isolating

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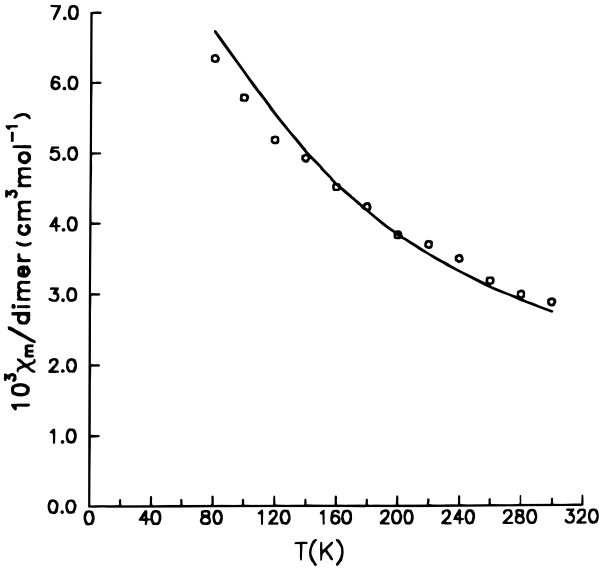

Figure 6. Plots of molar susceptibility (χ_M per dimer) versus temperature for solid samples of $[Cu_2L(OH)(H_2O)][ClO_4]_3 \cdot 2H_2O \cdot 0.5HCl$ (**3a**). The solid line results from a least-squares fit of the susceptibility data to eq 1. See the text for fitting parameters.

pure samples of **2b** in bulk quantity the solution-state magnetic moment value for this complex was not determined. For **3b** the corresponding value is 1.70 μ_B, which is appreciably lower than that observed in the solid state (1.98 μ_B).

(c) Magneto−Structural Correlations. It is well documented now that the type and magnitude of magnetic exchange interactions in dinuclear complexes depend on the bridge identity, the M- - -M separation, the bond angles at the bridging atoms, the dihedral angle between the planes containing the copper(II) ions, the metal−bridging ligand bond lengths, and the metal ion stereochemistry.[46] From the variable-temperature magnetic susceptibility data of **2a**,**b**, it is clear that in both the complexes the two copper(II) centers are antiferromagnetically coupled. However, the coupling is much more pronounced in the former phenoxo/hydroxodicopper(II) complex ($2J = -440$ cm^{-1}) than in the latter bis(μ-hydroxo)dicopper(II) complex ($2J = -258$ cm^{-1}).

A closer look at Table 1 reveals that, in both the complexes, the Cu- - - Cu distance, the stereochemistry around each Cu center, and the average Cu−OR−Cu bond angle at the bridging atoms are comparable. The metal−bridging ligand bond lengths are slightly longer for the phenoxo-/hydroxo-bridged complex **2a** than the dihydroxo-bridged complex **2b**. The fact is that the Cu_2O_2 unit in **2b** deviates more from planarity than that of **2a**. This difference can provide a reasonable explanation to the difference in the magnetic behavior of the two complexes. It can be suggested that the lesser coupling in **2b** is attributable to the fact that two copper(II) ions do not lie in one plane. When the metal ion moves into the plane, overlap between the metal-based $d_{x^2-y^2}$ orbitals and the oxygen-based sp^2 hybrid orbitals is increased. Since this σ framework represents the dominant pathway for the superexchange mechanism, the enhanced overlap should result in an increase in the antiferromagnetic interaction.

EPR Spectra. To substantiate the magnetic behavior of **3a**,**b** we investigated their EPR spectral properties. For **3a**, the room-temperature solid-state spectrum shows features typical for a tetragonal copper(II) ($g_{||} = 2.26$, $g_\perp = 2.06$, $A_{||} = 165$ G).[47] At 77 K in the solid-state as well as in CH_3CN solution, the signal is comparatively weak (cf. magnetic studies). Solid samples of **3b** at 300 K exhibit a broad signal ($g_{||} = 2.30$, $g_\perp = 2.07$, $A_{||} = 160$ G). At 77 K both in the solid state and in CH_3CN solution, the samples exhibited very weak signal with $g_{av} = 2.06$, suggesting weak coupling (cf. magnetic studies).

Solution-State Structure of the Phenoxo-/Hydroxo-Bridged Dicopper(II) Complex 2a by ^{1}H NMR Spectroscopy. To see whether the solid-state structure is retained in solution, ^{1}H NMR spectral behavior of **2a** was investigated in CD_3CN. The spectral behavior (the spectrum ranges from +26 to −6 ppm) in CD_3CN is shown in Figure S8, Supporting Information. It is obvious that the bridged structure of **2a** is retained in solution.

Summary/Overview. With the synthesis of an interesting series of *m*-xylyl-based ligands L (L′), L-NO_2, and L″, capable of providing only two nitrogen coordinations to each copper center, the oxygenation of the dicopper(I) complexes have been systematically investigated. Rapid decomposition to aromatic ring-hydroxylated product even at −80 °C implies that the energy barrier for conversion of intermediate dicopper(II)−peroxo to such species is small.

Several groups have tried to throw light on the oxygenation behavior as a function of the nature of solvent.[11−13] The observed higher hydroxylation yield in more polar solvent is probably due to better solvation of polar transition states and/or intermediates.[50]

The present studies pinpoint (i) the effect of ligand structure, i.e., a six-membered chelate ring-forming ligand (L) gives rise to aromatic ring hydroxylation whereas a five-membered chelate ring-forming ligand (L″) gives only irreversible oxidation, (ii) the effect of appropriate positioning (geometry) of the xylyl ring of the ligand, i.e., compared to L, the failure of the ligand L′ to undergo hydroxylation reaction, and (iii) the effect of solvent polarity, i.e., a less polar solvent such as CH_2Cl_2 at 298 K gives rise to both hydroxylated as well as unhydroxylated product whereas a more polar solvent such as CH_3CN or DMF gives only hydroxylated product, on the reactivity properties of present dicopper(I) complexes with molecular oxygen. Experiments to carefully look at a comparative kinetic data on i the solvent dependence and ii temperature dependence of the aromatic hydroxylation are being planned.

Acknowledgment. Financial support by the Department of Science and Technology and the Council of Scientific and Industrial Research, Government of India, is gratefully acknowledged. Our sincere thanks are due to Professor W. B. Tolman for extending his laboratory facilities to carry out isolation and characterization of dicopper(I) complexes and low-temperature oxygenation studies. We are grateful to Dr. Samiran Mahapatra for performing such key experiments. We thank Rajeev Gupta for technical assistance, Pulakesh Mukherjee for some preliminary experiments with the synthesis of L″, and Dr. Nishi Gupta for the synthesis of L′-OH.

Supporting Information Available: Mass spectra (FAB) of ligand L (from method A) (Figure S1), ^{1}H NMR spectrum of ligand L (from method B) (Figure S2), mass spectra (FAB) of L-OH (Figure S3), ^{1}H NMR spectrum of **1c** in CD_2Cl_2 (Figure S4), mass spectra (FAB) of **3a,b** (Figure S5), UV−vis spectra of **2a**,**b** in CH_3CN (Figure S6), acid/base titration of **3a** in CH_3CN (Figure S7), ^{1}H NMR spectrum of **2a** in CD_3CN (Figure S8), and magnetic data for **2a**,**b**, and **3a**,**b** (Tables S1−S4) (13 pages). Ordering information is given on any current masthead page.

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(50) The reaction resembles a simple electrophilic aromatic substitution and might be expected to proceed via a cationic intermediate akin to a "σ complex" that would be preferentially stabilized in polar solvent. We are grateful to one of the reviewers for suggesting this.