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Crossover from Antiferro- to Ferromagnetic Exchange Coupling in a New Family of Bis-(μ-Phenoxydido)dicopper(II) Complexes: A Comprehensive Magneto-Structural Correlation by Experimental and Theoretical Study

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Abstract

Five neutral bis(µ-phenoxydo)dicopper(II) complexes, \([\text{Cu}_2(L^{\text{Me,Me,Me}}_{\text{Me,Me,Et}})_2]\) (1), \([\text{Cu}_2(L^{\text{i-Pr,i-Pr,i-Pr}}_{\text{i-Pr,i-Pr,i-Pr}})_2]\cdot\text{CH}_2\text{Cl}_2\) (2), \([\text{Cu}_2(L^{\text{i-Pr,i-Pr,i-Pr}}_{\text{i-Pr,i-Pr,i-Pr}})_2]\cdot2\text{H}_2\text{O}\) (3), \([\text{Cu}_2(L^{\text{i-Bu,i-Pr}}_{\text{i-Bu,i-Pr}})_2]\) (4), and \([\text{Cu}_2(L^{\text{i-Bu,i-Pr}}_{\text{i-Bu,i-Pr}})_2]\cdot\text{H}_2\text{O}\) (5) have been synthesized and characterized by single crystal X-ray diffraction analyses, magnetic studies, and density functional theory (DFT) calculations, in which the ligands \(\text{H}_2L^{\text{Me,Me,Me}} = \text{N,}\text{N-bis(2-hydroxy-3,5-dimethylbenzyl)}\cdot\text{-N',N'-dimethyl-ethylene-1,2-diamine, H}_2L^{\text{Me,Me,Et}} = \text{N,}\text{N-bis(2-hydroxy-3,5-dimethylbenzyl)}\cdot\text{-N',diethyl-ethylene-1,2-diamine, H}_2L^{\text{i-Pr,i-Pr,i-Pr}} = \text{N,}\text{N-bis(2-hydroxy-3,5-diisopropylbenzyl)}\cdot\text{-N',diisopropylethylene-1,2-diamine, and H}_2L^{\text{i-Bu,i-Pr}} = \text{N,}\text{N-bis(2-hydroxy-3,5-di-tert-butyl-5-methyl-benzyl)}\cdot\text{-N',diisopropylethylene-1,2-diamine}\) contain the same [O,N,N,O]-donor atoms combination but differ in substituents at phenol rings and at an amino nitrogen atom. The effect of these remote substituents on the nature of exchange coupling interactions (ferromagnetic vs antiferromagnetic) between the copper(II) ions has been investigated. The average Cu-O-Cu angle, Cu-O-Cu-O torsion angle, and Cu…Cu separation in 1 – 5 are varied systematically by these remote ligand substituents in the range 98.6 – 83.3°, 26.0 – 46.5°, and 2.982 – 2.633 Å, respectively. As a result, the intramolecular spin-spin coupling in these complexes are changing gradually from strong antiferromagnetic \((J = -395 \text{ cm}^{-1})\), where \(\hat{\text{H}} = -J\hat{\text{S}}_1\hat{\text{S}}_2\) to moderate ferromagnetic \((J = +53.2 \text{ cm}^{-1})\) regime. The crossover angle at which the magnetic interaction changes from antiferromagnetic to ferromagnetic \((J = 0)\) is determined to be at ca. 87° for this series of dicopper(II) complexes. DFT calculations support the experimentally determined crossover angle and disclose various magneto-structural correlations in the series 1 – 5.
INTRODUCTION

Dinuclear copper(II) complexes with a Cu₂O₂ core generated by the bridging hydroxido, alkoxido, and phenoxido ligands have received wide interest in contemporary coordination chemistry because of their relevance to bioinorganic chemistry,¹ as well as in molecular magnetism.² Being a d⁹ system with S = 1/2 ground state, the magnetic behaviour of copper(II) complexes is relatively easier to handle, both from experimental and theoretical points of view.³ Bleaney and Bowers derived a theoretical expression for the magnetic exchange coupling in dinuclear copper(II) compounds for the first time⁴ and used that expression to explain magnetic properties and EPR signatures of a dimeric copper(II) acetate.⁵

Numerous exchange-coupled bi- and polynuclear transition metal complexes have since been extensively studied in order to determine magneto-structural correlations,⁶ which could ultimately lead to the rational design of novel materials with desired magnetic properties. Thus, a linear correlation between the exchange coupling constant (J) and Cu²⁺–O–Cu²⁺ bridge angle (θ) within a family of planar dihydroxido-bridged dicopper(II) complexes was demonstrated.⁷ A transition from antiferromagnetic to ferromagnetic coupling (J = 0) was predicted to occur at θ ~ 97º. The phenomenon is believed to be due to an “accidental orthogonality” of two copper-based magnetic orbitals resulting in a spin triplet ground state with minimized interelectronic repulsion. A similar correlation has been reported also for the alkoxo-bridged dicopper(II) complexes.⁸,⁹ Indeed, several theoretical approaches have been employed to investigate the magnetic behaviour of dicopper complexes and provide the structure-properties correlation starting by the purely qualitative approach involving the estimation of the energy splitting and finishing by more complex ab initio methods.¹⁰
Although many structurally characterized bis(µ-phenoxyido) dicopper(II) complexes are known, except of few examples, 11-13 the copper(II) ions in dimers are almost exclusively antiferromagnetically coupled. 14 There are some scattered investigations on a series of bis(µ-phenoxyido) dicopper(II) complexes 14c, 15 that reveal exclusively antiferromagnetic coupling. Thus, Thompson et al. 15 reported a linear relationship between the exchange coupling constant and phenoxide bridge Cu–OPh–Cu angle (θ). The extrapolation of the data to the ferromagnetic regime yielded the crossover point (J = 0) at θ ~ 77º, which is well below the angle reported for dihydroxido and dialkoxido complexes. 7-9 Sillanpää et al. 14c proposed a more realistic crossover angle θ of 89º extrapolating the antiferromagnetic coupling in a series of diphenoxido complexes towards the ferromagnetic regime. 13b Thus, the lack of compounds exhibiting ferromagnetic coupling constitutes a serious obstacle for the proper investigation of magneto-structural correlations, as reported for hydroxido- and alkoxo-bridged complexes. 7-9 A series of bis(µ-phenoxyido) dicopper(II) complexes revealing both antiferromagnetic and ferromagnetic coupling would be desired for precise magneto-structural correlations.

We have an ongoing project on the chemistry and reactivity of transition metal complexes involving phenol-based ligands. 16, 17 Herein we report a new family of bis-(µ-phenoxyido)dicopper(II) complexes 1 – 5 including five structurally similar tetradeptate diphenol ligands (Scheme 1). Different sets of ligand substituents exert different steric pressure on the participating copper centers, which allows a large modulation of both structural parameters and magnetic properties in the series. Ultimately, we have been able to obtain antiferromagnetically and ferromagnetically spin-coupled complexes and consequently derive a precise magneto-structural correlation in bis-(µ-phenoxyido)dicopper species. The structural requirements for a crossover point (J = 0) have been determined precisely by interpolating magnetic data for the
first time. Density Functional Theory (DFT) calculations were also made to understand the magneto-structural correlations.

**EXPERIMENTAL SECTION**

**Materials.** All reactions were carried out in aerobic environment with chemicals available from commercial sources and used as received. The solvents were reagent grade, dried by standard procedure,\(^{18}\) and distilled under nitrogen prior to their use. The tetradentate bis-phenol ligands were prepared following a reported procedure\(^{19}\) with minor modification. The protocol involves a Mannich type condensation reaction between a 2,4-substituted dialkylphenol and \(N,N\)-dialkyl ethylenediamine as outlined below. Altogether five ligands have been synthesized, all having \(N_2O_2\) donor combination but differ among themselves by the steric hindrance offered by the substituents \(R_1, R_2\) and \(R_3\) combinations which is systematically varied in going from \(H_2L^{Me,Me,Me}\) to \(H_2L^{t-Bu,t-Bu,i-Pr}\) as summarized in Scheme 1.

**Synthesis of Ligands.** A modified procedure for the synthesis of \(N,N\)-bis(2-hydroxy-3,5-dimethylbenzyl)-\(N',N'\)-dimethylethylenediamine-1,2-diamine, \((H_2L^{Me,Me,Me})\) is described here as a prototype. To a solution of 2,4-dimethyl phenol (2.44 g, 20 mmol) in methanol (30 mL) were added \(N,N\)-dimethylethylenediamine (0.88 g, 10 mmol) and paraformaldehyde (60 mg, 20 mmol). The resulting solution was refluxed for 15 hr. It was then cooled to room temperature and rotary evaporated to ca 10 mL volume. The resulting white precipitate was filtered off, washed with 20 mL of cold methanol and re-crystallized from dichloromethane/methanol (1:1 v/v) mixture. Yield: 80%; mp 174 °C. Anal. Calc. for \(C_{22}H_{32}N_2O_2\): C, 74.12; H, 9.05; N, 7.86. Found: C, 74.28; H, 9.19; N, 7.85%. \(^1\)H NMR (400 MHz, CDCl\(_3\), TMS, \(\delta/\)ppm): 2.20 (s, 12H, of \(C\)H\(_3\)), 2.30 (s, 6H, of \(N(C\)H\(_3\))\(_2\)), 2.55 (s, 4H, of \((C\)H\(_3\))\(_2\)N–(\(C\)H\(_2\))\(_2\)–), 3.57 (s, 4H, \(Ar\)--C\(_2\)H\(_3\)), 6.67
(d, 2H, aryl), 6.85 (d, 2H, aryl), 9.46 (broad, 2H, OH). ESI−MS (positive) in CH₃CN: m/z = 357.55 (100%, M+H⁺).

Other N₂O₂ ligands have been synthesized following the same procedure. N,N-bis(2-hydroxy-3,5-dimethylbenzyl)-N',N'-diethyleneglycol-1,2-diamine, (H₂L¹,Me,Me,Et). Yield: 82%; mp 170 °C. Anal. Calcd for C₂₄H₃₆N₂O₂: C, 74.96; H, 9.44; N, 7.28. Found: C, 74.90; H, 9.64; N, 7.34%. ¹H NMR (400 MHz, CDCl₃, TMS, δ/ppm): 1.11 [t, 6H, CH₃ of N(CH₂CH₃)₂], 2.19 [s, 12H, CH₃ of Ph(CH₃)₂], 2.53 (q, 4H, CH₂ of N(CH₂CH₃)₂), 2.62 (t, 4H, CH₂ of (Et)₂N−(CH₂)₂−), 3.56 (s, 4H, Ar−CH₂), 6.68 (s, 2H, aryl), 6.85 (s, 2H, aryl), 9.32 (broad, 2H, OH). ESI−MS (positive) in CH₃CN: m/z = 385.4 (100%, M+H⁺).

N,N-bis(2-hydroxy-3,5-diisopropylbenzyl)-N',N'-diisopropylethylene-1,2-diamine, (H₂L¹,Pr,Pr,Pr). Yield: 65%; mp 158 °C. Anal. Calcd for C₃₄H₅₆N₂O₂: C, 77.81; H, 10.76; N, 5.34. Found: C, 77.88; H, 10.64; N, 5.34%. ¹H NMR (400 MHz, CDCl₃, TMS, δ/ppm): 1.03 [d, 12H, CH₃ of N(CH(CH₃)₂)₂], 1.20 [d, 24H, CH₃ of Ph(CH(CH₃)₂)₂], 2.55 [t, 2H, CH₂ of (i-Pr)₂N−CH₂−CH₂−N(R)₂], 2.73 [t, 2H, CH₂ of (i-Pr)₂N−CH₂−CH₂−N(R)₂], 2.88 [m, 2H, CH of p-Ph(CH(CH₃)₂)₂], 3.15 [m, 2H, CH of o-Ph(CH(CH₃)₂)₂], 3.29 [m, 2H, CH of N(CH(CH₃)₂)₂], 3.60 (s, 4H, Ar−CH₂), 6.71 (d, 2H, aryl), 6.93 (d, 2H, aryl). ESI−MS (positive) in CH₃CN: m/z = 525.5 (100%, M+H⁺).

N,N-bis(2-hydroxy-3-tert-butyl-5-methylbenzyl)-N',N'-diisopropylethylene-1,2-diamine, (H₂L¹,Bu,Me,Pr). Yield: 62%; mp 162 °C. Anal. Calcd for C₃₂H₅₂N₂O₂: C, 77.37; H, 10.55; N, 5.64. Found: C, 77.90; H, 10.38; N, 5.59%. ¹H NMR (400 MHz, CDCl₃, TMS, δ/ppm): 1.05 [d, 12H, CH₃ of N(CH(CH₃)₂)₂], 1.36 (s, 18H, CH₃ of t-butyl), 2.22 [s, 6H, CH₃ of Ph(CH₃)], 2.24 [t, 2H, CH₂ of (i-Pr)₂N−CH₂−CH₂−N(R)₂], 2.77 [t, 2H, CH₂ of (i-Pr)₂N−CH₂−
\[ \text{CH}_2\text{-N}(R)\text{]} \], 3.24 [m, 2H, CH of N{\text{CH(\text{CH}_3)}\text{]}\text{]}, 3.52 (s, 4H, Ar–CH\text{)}, 6.68 (d, 2H, aryl), 6.96 (d, 2H, aryl). ESI–MS (positive) in CH\text{3}CN: \text{m/z} = 497.8 (100\%, \text{M+H}^+).

\[ \text{N,N-bis(2-hydroxy-3,5-di-tert-butylbenzyl)-N',N'-diisopropylethylene-1,2-diamine,} \]
(\text{H}_2\text{L}^{t\text{-Bu},t\text{-Bu},i\text{-Pr)}\text{)}. Yield: 55\%; mp 165 °C. Anal. Calcd for C\text{38}H\text{64}N\text{2}O\text{2}: C, 78.57; H, 11.10; N, 4.82. Found: C, 78.50; H, 11.01; N, 4.80\%. \text{^1}H NMR (400 MHz, CDCl\text{3}, TMS, \delta/ppm): 1.07 \{d, 12H, CH\text{3} of N(\text{CH(\text{CH}_3)}\text{]}\text{]}, 1.27 (s, 18H, CH\text{3} of t-butyl), 1.38 (s, 18H, CH\text{3} of t-butyl), 2.59 [t, 2H, CH\text{2} of (i-Pr)\text{2}N–CH\text{2}-\text{N}(R)\text{]}\text{]}, 2.79 [t, 2H, CH\text{2} of (i-Pr)\text{2}N–\text{CH}(\text{CH}_2\text{)}\text{-CH}\text{_2}-\text{N}(R)\text{]}\text{]}, 3.27 [m, 2H, CH of N{\text{CH(\text{CH}_3)}\text{]}\text{]}, 3.58 (s, 4H, Ar–CH\text{)}, 6.69 (d, 2H, aryl), 7.18 (d, 2H, aryl) 8.82 (broad, OH). ESI–MS (positive) in CH\text{3}CN: \text{m/z} = 581.8 (100\%, \text{M+H}^+).

\text{Preparation of Complexes. Safety Note! Perchlorate salts of metal complexes are potentially explosive and should be handled in small quantities with sufficient care.}\text{[20]}

\[ [\text{Cu}_2(L^{\text{Me},\text{Me},\text{Me}})\text{]}\text{]}\text{ (1).}\] The ligand \text{H}_2L^{\text{Me},\text{Me},\text{Me}} (89 mg, 0.25 mmol) was dissolved in methanol (30 mL). To this were added Et\text{3}N (68 \mu\text{L}, 0.50 mmol) and \text{Cu(ClO}_4)_2\text{}·\text{6H}_2\text{O (90 mg, 0.25 mmol). The resulting dark brown solution was refluxed for 2 h and filtered over a celite bed. The filtrate solution was left in the air for slow evaporation. The product was obtained as a brown crystalline solid within 2 - 3 days. The crystals were filtered off, washed with cold methanol and air dried. Some of these crystals were of diffraction quality and used directly for X-ray crystal structure analysis. Yield: 70 mg (65\%). Anal. Calcd for C\text{44}H\text{60}N\text{4}O\text{4}Cu\text{2}: C, 63.21; H, 7.23; N, 6.70. Found: C, 63.25; H, 7.26; N, 6.67\%. FT-IR bands (KBr pellet, cm\text{−1}): 2956(m), 1610(m), 1477(s), 1321(m), 1249(m), 1161(m), 858(m), 800(m). UV–vis (\text{CH}_2\text{Cl}_2) [\lambda_{\text{max}}/\text{nm (ε, L mol}^{-1} \text{cm}^{-1})]: 412(5100), 473(3900), 640(880).
**[Cu₂(LMe,Me,Et)₂]·CH₂Cl₂ (2).** Complex 2 was synthesized following a similar procedure as that described above for 1 using the ligand H₂LMe,Me,Et and CuCl₂·2H₂O as metal ion precursor instead of Cu(ClO₄)₂·6H₂O. The compound was recrystallized from 1:1 (v/v) dichloromethane/methanol mixture. The compound is prone to solvent loss. Drying under vacuum for a long time afforded a fully desolvated analytical-grade sample that was used subsequently for microanalysis. Yield: 60%. Anal. Calcd for C₄₈H₆₈N₄O₄Cu₂: C, 64.62; H, 7.68; N, 6.28. Found: C, 64.66; H, 7.83; N, 6.27%. FT-IR bands (KBr pellet, cm⁻¹): 2918(m), 1610(m), 1473(s), 1321(m), 1245(m), 1159(m), 858(m), 798(m). UV−vis (CH₂Cl₂) [λₓₘₐₓ / nm (ε, L mol⁻¹ cm⁻¹)]: 410(4900), 474(3600), 636(980).

**[Cu₂(Li-Pr,i-Pr,i-Pr)]₂·2H₂O (3).** Complex 3 was synthesized in a manner similar to that for 1 using the ligand H₂Li-Pr,i-Pr,i-Pr. The crystals were obtained by slow evaporation of the resulting methanol solution. We also used a desolvated sample for microanalysis as we did for compound 2. Yield: 55%. Anal. Calcd for C₆₈H₁₀₈N₄O₄Cu₂: C, 69.65; H, 9.28; N, 4.78. Found: C, 68.83; H, 9.19; N, 4.76%. FT-IR bands (KBr pellet, cm⁻¹): 2958(s), 1608(m), 1467(s), 1315(m), 1234(m), 881(m), 783(m). UV−vis (CH₂Cl₂) [λₓₘₐₓ / nm (ε, L mol⁻¹ cm⁻¹)]: 426(6800), 634(1500), 775(1050).

**[Cu₂(Lt-Bu,Me,i-Pr)]₂ (4).** Complex 4 was synthesized in a manner similar to that described above for 1 using the ligand H₂L₄-Bu,Me,i-Pr. The crystals were grown by slow evaporation of the resulting methanol solution. Yield: 40%. Anal. Calcd for C₆₄H₁₀₀N₄O₄Cu₂: C, 68.84; H, 9.03; N, 5.02. Found: C, 68.75; H, 9.11; N, 5.07%. FT-IR bands (KBr pellet, cm⁻¹): 2960(s), 1608(m), 1465(m), 1271(m), 1236(m), 1151(m), 858(m), 813(m). UV−vis (CH₂Cl₂) [λₓₘₐₓ / nm (ε, L mol⁻¹ cm⁻¹)]: 435(5400), 658(1250), 830(630).
\[ \text{[Cu}_2(L^{t-Bu,t-Bu,i-Pr})_2]\cdot\text{H}_2\text{O (5)} \] Complex 5 was prepared in a manner similar to that for 1 using the ligand \( \text{H}_2L^{t-Bu,t-Bu,i-Pr} \). Crystalline product was separated from the solution during the course of refluxing. Some of these crystals were of diffraction quality and used directly for X-ray crystal structure analysis. We used a desolvated sample for microanalysis as we did for compound 2. Yield: 54%. Anal. Calcd for \( \text{C}_{76}\text{H}_{124}\text{N}_4\text{O}_4\text{Cu}_2 \), C, 71.04; H, 9.73; N, 4.36. Found: C, 70.92; H, 9.44; N, 4.34%. FT-IR bands (KBr pellet, cm\(^{-1}\)): 2958(s), 1604(m), 1471(s), 1301(m), 1238(m), 877(w) 820(w). UV–vis (CH\(_2\)Cl\(_2\)) \([\lambda_{\text{max}} / \text{nm (ε, L mol}^{-1} \text{ cm}^{-1})]\): 434(5300), 533(2500), 661(1400), 840(870).

**Physical Measurements.** IR spectroscopic measurements were made on samples pressed into KBr pellets using a Shimadzu 8400S FT-IR spectrometer while for UV-visible spectral measurements; a PerkinElmer Lambda 950 UV/vis/NIR spectrophotometer was employed. Elemental analyses (for C, H and N) were performed at IACS on a PerkinElmer model 2400 Series II CHNS Analyzer. The electrospray ionization mass spectra (ESI–MS) in positive ion mode were measured on a Micromass QTOF model YA 263 mass spectrometer. The \(^1\)H NMR spectra were recorded on a Bruker model Avance DPX-400 spectrometer using SiMe\(_4\) as internal reference. Magnetic susceptibility data were collected with a Quantum Design MPMS-XL SQUID magnetometer working between 1.8 – 350 K with the magnetic field up to 7 Tesla. The data were corrected for the sample holder and the diamagnetic contributions calculated from the Pascal's constants.\(^\text{21}\)

**Theoretical Calculations.** Program ORCA 4.0.0.2 was used for all spin-unrestricted DFT calculations.\(^\text{22}\) The calculations were performed on molecular structures as obtained from crystallography without further optimizations. Single point calculations were done with B3LYP
functional\textsuperscript{23,24} using def2-SVP and def2-TZVP basis sets\textsuperscript{25} for C/H and non-C/H atoms, respectively. RIJCOSX approximation with appropriate auxiliary basis sets (def2/J)\textsuperscript{26} were employed for all calculations. Magnetic coupling was analyzed using broken-symmetry formalism\textsuperscript{27-29} Corresponding orbitals were used to visualize molecular magnetic orbitals.\textsuperscript{30} Molecular orbitals and spin density maps were visualized with Molekel.\textsuperscript{31}

**X-ray Crystallography.** Suitable crystals of 1 (brown block, 0.14×0.12×0.08 mm\textsuperscript{3}), 2 (brown block, 0.16×0.12×0.09 mm\textsuperscript{3}), 3 (brown block, 0.10×0.09×0.08 mm\textsuperscript{3}), 4 (brown block, 0.16×0.15×0.10 mm\textsuperscript{3}) and 5 (brown block, 0.12×0.08×0.06 mm\textsuperscript{3}) were mounted on glass fibres coated with perfluoropolyether oil before mounting. Intensity data for the aligned crystals were measured employing a Bruker SMART APEX II CCD diffractometer equipped with a monochromatized Mo K\textsubscript{α} radiation (\(\lambda = 0.71073\) Å) source at 150(2) K except for compound 2 which was measured at 293(2) K. No crystal decay was observed during the data collections. In all cases, absorption corrections based on multiscans using the SADABS software\textsuperscript{32} were applied. The structures were solved by direct methods\textsuperscript{33} and refined on F\textsuperscript{2} by a full-matrix least-squares procedure based on all data minimizing wR = [\(\sum\left(w\left(F_0^2 - F_c^2\right)^2\right) / \sum(F_0^2)^2\)]\textsuperscript{1/2}, R = \(\sum |F_0| - |F_c| / \sum|F_0|\), and S = [\(\sum[w\left(F_0^2 - F_c^2\right)^2] / (n - p)\)]\textsuperscript{1/2}. SHELXL-2013 was used for both structure solutions and refinements.\textsuperscript{34} A summary of the relevant crystallographic data and the final refinement details are given in Table 1. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and isotropically fixed in the final refinement [d(C–H) = 0.95 Å, with the isotropic thermal parameter of U\textsubscript{iso}(H) = 1.2 U\textsubscript{iso}(C)]. The SMART and SAINT software packages\textsuperscript{35} were used for data collection and reduction, respectively. Crystallographic diagrams were drawn using the DIAMOND software package.\textsuperscript{36}
RESULTS AND DISCUSSION

Syntheses. Five tetradebate amino-bis phenol ligands \( \text{H}_2\text{L}^{R_1,R_2,R_3} \) with closely related structures have been synthesized in moderate to high yields by Mannich type of condensation reaction between \( N,N \)-dialkylethylene diamine and 2,4-dialkylphenol (Scheme 1). These ligands in aerobic environment (with the exception of \( \text{H}_2\text{L}^{\text{Me,Me,Et}} \)) combine with \( \text{Cu(ClO}_4)_2 \cdot 6\text{H}_2\text{O} \) in refluxing methanol in the presence of an added base (\( \text{NEt}_3 \)) to generate the neutral bis-(\( \mu \)-phenoxido)dicopper(II) complexes (1, 3–5) having a planar \( \text{Cu}_2\text{O}_2 \) core (Scheme 2) as revealed from X-ray crystallography (vide infra). We have failed to isolate compound 2 in the crystalline form following the same procedure using the ligand \( \text{H}_2\text{L}^{\text{Me,Me,Et}} \). Interestingly however when \( \text{Cu(ClO}_4)_2 \cdot 6\text{H}_2\text{O} \) was replaced by \( \text{CuCl}_2 \cdot 2\text{H}_2\text{O} \) as the metal ion precursor, we were able to isolate 2 in the crystalline form.

The Cu(II) centers in compounds 1 and 2 present a square pyramidal geometry. We have deliberately chosen to introduce three different substituents \( R_1 \), \( R_2 \), and \( R_3 \) in the ligand framework in order to influence the coordination geometry around the individual copper centers. Such strategy appears to be successful since the copper centers in the later three compounds 3, 4, and 5 appear to be square planar (Scheme 2) as one of the donor amino nitrogen atoms is forced to stay away from coordination due to larger steric constrains exerted by a bulky \( R_3 \) substituent like \( i\)-Pr. Similarly, the remaining substituents \( R_1 \) and \( R_2 \) attached to the phenolate rings of the coordinated ligands also have their cumulative influence on the crystal structures of compounds 1 and 3–5. Juxtaposition of the steric influence of all these substituents has an overall effect in tuning the average Cu–O–Cu bridge angles in the reported compounds.
Description of Crystal Structures

A slightly different crystal structure of compound $[\text{Cu}_2(\text{L}^{\text{Me,Me,Me}})_2]$ 1 was reported earlier. The methodology adopted for the synthesis of that compound was also different. In our hand, the complex crystallizes in the orthorhombic space group $Pnna$ with four molecular mass units accommodated per unit cell. The molecule has a two-fold symmetry and the asymmetric unit contains half of the complex molecule, i.e. one crystallographic copper site. A perspective view of the molecular structure of 1 is displayed in Figure S1 (in the Supporting Information) and the relevant metrical parameters along with those of compounds 2 - 5 are summarized in Tables 2 and 3. The coordination geometry around the individual copper center is distorted square pyramidal with a $\tau$ parameter of 0.23. The basal plane around the Cu center is completed by the phenolate oxygen atom O1, bridging phenolate oxygen O2 and the amino nitrogen atom N1 all coming from the tetradeutent N$_2$O$_2$ ligand along with the bridging phenolate oxygen O2', coming from another ligand attached to the adjacent metal center. The apical site is coordinated by the remaining amino nitrogen atom N2 of the N$_2$O$_2$ ligand. The basal planes around the adjacent copper atoms (Cu1, O1, O2, N1, O2' plane) form a folded geometry with a roof angle of 58.55°. The phenyl rings are rotated with respect to the Cu$_2$O$_2$ plane and form a dihedral angle of 56.75°. The intramolecular Cu⋯Cu separation and the Cu1-O-Cu2 bridge angle of the Cu$_2$O$_2$ core are 2.9822(16) Å and 98.63(17)°, respectively. The trans angles O1-Cu1-O3 (165.15(18)°) and O2-Cu1-N1 (151.36(19)°) in the basal plane are appreciably short of linearity, indicating a slightly compressed basal plane and the Cu ions are displaced out (by 0.248 Å) of these planes towards the apical nitrogen atoms. The crystal packing analysis indicates that the shortest Cu⋯Cu intermolecular distance is equal to 8.339(2) Å confirming that the complexes are well isolated.
Compound [Cu$_2$(L$^{Me,Me,Et}$)$_2$]·CH$_2$Cl$_2$ 2 crystallizes in the triclinic space group $P$-1 with two complexes per unit cell which also contains one dichloromethane molecule as solvent of crystallization. The asymmetric unit of 2 consists of a dinuclear Cu$_2$L$_2$ molecule with two phenolatate O atoms acting as a (μ-O)$_2$ bridge between the crystallographically independent metal centers. The H$_2$L$^{Me,Me,Et}$ ligand coordinates as a (L$^{Me,Me,Et}$)$_2^-$ anion in a tetradeinate/bridging manner through the two phenolate oxygen atoms and nitrogen atoms of the amino groups. A perspective view of the molecular structure is presented in Figure 1. The coordination geometry around the two copper atoms is distorted square pyramidal with $\tau$ values$^{38}$ of 0.35 and 0.09 for Cu1 and Cu2, respectively; indicating different degrees of distortion around the two metal sites. The basal plane around the copper atom Cu1 is completed by one phenolate oxygen O1, one amino nitrogen N1 and two bridging phenolate oxygen atoms O2 and O3. Corresponding donor atoms around Cu2 are O4, N3, O3, O2, respectively. The apical site around these metal centers is taken up by the remaining amino nitrogen N2 and N4, respectively. The distances of the axial N atoms from the metal centers Cu1 and Cu2 are 2.503(3) and 2.429(2) Å, respectively, which are more elongated compared to the corresponding distance 2.392(5) Å found in complex 1. The observed dihedral angle (61.73°) between the two basal planes indicates a folded syn-clinial arrangement. The Cu1 and Cu2 atoms are displaced from their respective basal planes by 0.290 and 0.241 Å, respectively. The intramolecular Cu···Cu separation and the average Cu1-O-Cu2 bridge angle of the Cu$_2$O$_2$ core are 2.993(4) Å and 97.92°, respectively. The average dihedral bridge angle between the phenoxy plane and Cu$_2$O$_2$ plane is 58.48°. The shortest Cu···Cu intermolecular distance is longer than in 1 and equal to 12.820(7) Å.

Compound [Cu$_2$(L$^{i-Pr,i-Pr,i-Pr}$)$_2$]·2H$_2$O 3 crystallizes in the monoclinic space group $P2_1/c$ with four molecular mass units accommodated per unit cell. It contains two water molecules as
solvent of crystallization. A perspective view of the molecular structure of 3 is displayed in Figure 2a. Unlike the previous two compounds, the ligands coordinate in a tridentate/bridging manner to the individual copper centres. The steric constraints of the bulkier iso-propyl groups enforce the amino nitrogen atoms N2 and N4 of the ligands (Figure 2a) to stay away from coordination. The Cu centers thus have square planar geometry in this compound. Its relevant metrical parameters are summarized in Table 2. The basal plane around the copper atoms are completed by one phenolate oxygen, one amine nitrogen and two bridging phenolate oxygen atoms [O1, N1, O2, O3 around Cu1 and O2, O3, O4, N3 around Cu2]. The trans angles at the copper centers lying in the range of 165.4 -170.0° indicate a distorted square-planar nature of the metal ion geometry. The dihedral angle between the two basal planes around the copper atoms is 46.98° (Figure 2b). The intramolecular Cu⋯Cu separation and the average Cu1-O-Cu2 angle of the Cu2O2 core are 2.866(2) Å and 94.39°, respectively. The Cu1 and Cu2 atoms are displaced from the basal planes by 0.013 and 0.055 Å, respectively. The average dihedral angle between the phenoxo plane and Cu2O2 plane for this molecule is 51.26°. The shortest Cu⋯Cu intermolecular distance is found to be equal to 10.598(3) Å.

Compound [Cu2(L-t-Bu,Me,i-Pr)2] 4 crystallizes in the triclinic space group P-1 with two complexes accommodated per unit cell. A perspective view of the molecular structure of 4 is displayed in Figure 3. Important metrical parameters are presented in Table 2. Here also the coordination geometry around the two copper centers is distorted square planar and the trans angles around the copper centers in the basal planes vary from 165.32 to 169.32°. The dihedral angle of 76.55° between the two basal planes also indicates a folded syn-clinial arrangement. The Cu(1) and Cu(2) ions are displaced from the basal planes by 0.150 and 0.158 Å, respectively. The intramolecular Cu⋯Cu separation and the average Cu1-O-Cu2 angle of the Cu2O2 core are
2.7204(4) Å and 86.945°, respectively. The average dihedral angle between the phenoxy plane and Cu$_2$O$_2$ plane for this molecule is 73.36°, while the shortest Cu···Cu intermolecular distance is equal to 11.876(1) Å.

Compound [Cu$_2$(L$^{t$-Bu,$t$-Bu,$i$-Pr)$_2$]$\cdot$H$_2$O 5 crystallizes in the monoclinic space group C2/c with eight molecular mass units accommodated per unit cell. This compound has an almost similar structure (Figure S2) as that of complex 4. The influence of the associated dianionic ligand H$_2$L$^{t$-Bu,$t$-Bu,$i$-Pr} with bulkier substituent combination has important ramification on the overall structural parameters as summarized in Table 2. The dihedral angle between the two basal planes around copper atoms is 80.96°. The intramolecular Cu···Cu separation and the average Cu1-O-Cu2 angle of the Cu$_2$O$_2$ core are 2.633(1) Å and 83.27°, respectively. The later value is probably the shortest Cu-O-Cu bridge angle, reported thus far in the literature for a bis(μ-phenoxyido) dicopper(II) complex. The average dihedral angle between the phenoxy plane and Cu$_2$O$_2$ plane for this molecule is 68.69°. The Cu1 and Cu2 atoms are displaced from the basal planes by 0.147 and 0.149 Å, respectively while the shortest Cu···Cu intermolecular distance is 11.010(1) Å.

A gradual increase in the steric bulk of the substituents on the ligand's N atom enforces the Cu centers in these dinuclear copper complexes to adopt a square planar geometry in 3 – 5 instead of a square pyramidal geometry observed in 1 and 2. The combinations of substituent thus have a modest to large influence in tuning the Cu···Cu separations, bridging Cu-O-Cu bond angles, and hinge distortion of the Cu$_2$O$_2$ framework (Cu-O-Cu-O torsion angle) as summarized in Table 3.
Electronic Spectra. The electronic spectra of these compounds were recorded in dichloromethane solution. All complexes exhibit strong absorption bands in 412–434 nm region due to phenolate to metal charge transfer transitions. Much weaker bands in 636–661 nm region were assigned to d-d transitions (Figure 4). Upon increasing the steric crowding of the substituents at the phenol ring, the ligand to metal charge transfer band exhibits a bathochromic shift (Table 4) due to an enhanced charge transfer from phenolate to metal ion concomitant with the increase of the inductive effect.

Magnetic Properties. Magnetic properties of the complexes 1 – 5 were investigated using a SQUID magnetometer working between 1.8 and 350 K up to 7 T. The temperature dependence of $\chi T$ for all compounds is reported in Figure 5. The room temperature $\chi T$ values are equal to 0.39, 0.49, 0.70, 0.84, and 0.81 cm$^3$ mol$^{-1}$ K for compounds 1, 2, 3, 4, and 5, respectively. For compounds 4 and 5, these values are in good agreement with the theoretical value of 0.82 cm$^3$ mol$^{-1}$ K expected for two non-interacting copper(II) ions ($S = 1/2$; $g = 2.1$). In the case of the three former compounds 1 – 3, the observed lower $\chi T$ values originate from the occurrence of antiferromagnetic interactions, which are still operative at room temperature. Such fact is further confirmed by the decrease of $\chi T$ upon cooling, reflecting strong dominant antiferromagnetic interactions. At low temperature, the zero $\chi T$ value for complexes 1 – 3 points out a diamagnetic ground state. In contrast, the temperature dependence of $\chi T$ for complexes 4 and 5 shows a positive deviation upon cooling due to the presence of ferromagnetic interactions to reach a maximum close to 10 K before decreasing at low temperature, most likely due to intermolecular interactions. The maximum $\chi T$ values of 1.13 and 1.02 cm$^3$ mol$^{-1}$ K for 4 and 5, respectively, are close to the value of 1.10 cm$^3$ mol$^{-1}$ K expected for a $S = 1$ species ($g = 2.1$)
resulting from a ferromagnetic coupling between the spin carriers. Such ferromagnetic interaction is ultimately confirmed by monitoring the field dependence of magnetization at 1.8 K (Figure 6), which can be fitted with a Brillouin function for a $S = 1$ species ($g = 2.30 \pm 0.02$ and $2.10 \pm 0.02$ for 4 and 5, respectively).

To get further details, the exchange interaction between the two Cu(II) ions can be extracted using the isotropic Hamiltonian, $\hat{H} = -J\hat{S}_1\hat{S}_2$, leading to the well-known Bleaney-Blowers equation.\textsuperscript{5} Using the PHI software,\textsuperscript{40} the thermal dependence of $\chi T$ as well as the magnetization curves for 4 and 5 were fitted. Note that for 4 and 5, an intermolecular interaction parameter was taken into account, while for 2, both a temperature independent paramagnetism (TIP) contribution and intermolecular parameter were taken into account. The parameters from the best fits are reported in Table 5. It could be noticed that for 2, the weak value of the gyromagnetic factor may reflect the presence of a small impurity. Yet, the slope of $\chi T$ vs. $T$ being mainly affected by the exchange interaction, the extracted constant could be considered as meaningful.

The nature of the magnetic exchange interactions in phenoxido dinuclear complexes has been largely studied.\textsuperscript{14a} Thus, there are several parameters affecting the magnitude and sign of the $J$ parameter such as: the value of Cu-O-Cu angle, the Cu...Cu and Cu–O distances,\textsuperscript{41} as well as the distortion of the copper ion geometry,\textsuperscript{42} the effect of the asymmetry in the Cu-hydroxo bond and the out-of-plane displacement of the hydrogen atoms of the hydroxo- bridge.\textsuperscript{9} Noticeably, there are only limited examples of phenoxido-bridged dinuclear copper complexes that exhibit ferromagnetic interactions.\textsuperscript{11-13} It appears that one of the main factors controlling the sign of the exchange interactions is the Cu-O-Cu bridging angle, which is correlated with the
geometry of the Cu(II) ion.\textsuperscript{12,14c,43} In the case of hydroxo-bridged dicopper(II) complexes, it was experimentally evidenced that $J$ varies linearly with this bridging angle through the Hatfield and Hodgson relationship.\textsuperscript{7a} A transition from antiferromagnetic to ferromagnetic coupling is therefore expected for a Cu-O-Cu angle smaller than $97^\circ$.

In the wide majority of the reported phenoxido systems, the magnetic interaction is found to be antiferromagnetic due to the important bridging angle. Thus, the complexes 1 – 3 exhibit common antiferromagnetic interactions with the magnitude of $J$, which increases as the Cu-O-Cu angle increases. Reducing this angle induces the switching to moderate ferromagnetic interactions. In our present systems, the crossover is found for angle ($\theta$) around $87^\circ$ (Figure 7). This value is in good agreement with the value of $90^\circ$ previously reported.\textsuperscript{11} However, we would like to point out that the strength of this ferromagnetic coupling is way larger than in other reported complexes due to smaller Cu-O-Cu angle in our systems. This can be ascribed to short Cu…Cu distance and a large hinge distortion of the Cu$_2$O$_2$ core leading to large Cu-O-Cu-O torsion angle (the average dihedral angle between the Cu$_2$O$_2$ plane and the bridging phenoxy aromatic ring plane). A switch from antiferromagnetic to ferromagnetic regime in our series can be estimated to occur at Cu…Cu distance of 2.71 Å (Figure S3) and at Cu-O-Cu-O torsion angle of $42^\circ$ (Figure S4). It could however be noticed, that below the crossing point, the magnitude of the ferromagnetic interaction is less dependent towards the angle’s change.

Of particular interest in compounds 1- 5 are the different alkyl substituents (R1, R2 and R3) with similar Hammet parameters in their ligand frameworks that support a high quality correlation, spanning a transformation from antiferro- to ferromagnetic range.

**Theoretical Calculations.** Density functional theory (DFT) calculations were performed on complexes 1 – 5. The exchange coupling constants were calculated using a broken-symmetry
To preserve all subtle geometrical features that can heavily influence spin coupling, calculations were performed using molecular structures as determined by X-ray crystallography (vide supra) without optimization.

The calculated antiferromagnetic coupling constants in 1 – 3 are in excellent agreement with experimentally obtained values (Table 6). Although we were able to reproduce ferromagnetic coupling in 4 and 5, its strength is underestimated in our calculations. In spite of considerably differing molecular structures in the series 1 – 5, the Cu–Cu coupling seems to correlate with a Cu–O–Cu angle. Similarly, to related species, a roughly linear correlation can be obtained (Figure 8). Thus, a crossing point of 86° corresponding to the change of the sign of the coupling constant has been obtained in our calculations. This value is in very good agreement with the experimentally obtained correlation (Figure 7) and previously reported data on related species.

Interestingly, the coupling in 1 – 5 correlates with a hinge distortion of the Cu$_2$O$_2$ core expressed as a Cu–O–Cu–O torsion angle. Surprisingly, a linear correlation of similar quality was obtained in this case (Figure 9). These findings point to the fact that Cu–O–Cu angle and Cu–O–Cu–O torsion angle might also correlate over the whole range in our series. Indeed, an excellent linear correlation ($R^2 = 0.995$) between these two structural parameters could be obtained (Figure 10). Thus, although both the decrease of Cu–O–Cu angle and the increase of Cu–O–Cu–O torsion angle are known to promote ferromagnetic coupling in bis(phenoxido)-bridged dicopper(II) complexes, here we have disclosed a correlation between those structural parameters for the first time. Further, we have analyzed the geometry of all similar known bis(phenoxido)dicopper complexes that are non-planar: they feature phenylene-CH$_2$-N(R)-CH$_2$-
phenoxides and Cu-O-Cu-O torsion angles of non-zero. A similar linear correlation, albeit of lower quality ($R^2 = 0.88$) has been obtained for those data (Figure. S5). The fit is exceptionally good for structures with Cu-O-Cu-O angles higher than $10^\circ$ and Cu-O-Cu angles lower than $100^\circ$. For more flat structures with Cu-O-Cu-O angles below $10^\circ$, the data become spread significantly.

The antiferromagnetic coupling between two copper d($x^2-y^2$) type orbitals in 1 – 3 is promoted by superexchange interactions through in-plane p-orbitals of bridging oxygen atoms (Figures 11, S6 and S7). Such antiferromagnetic coupling is common for this class of compounds.\textsuperscript{14a} However, relatively strong ferromagnetic coupling in 4 and 5 is rather unusual. Here, antiferromagnetic pathway by superexchange via bridging oxygen becomes significantly diminished (Figures 12, S8). Besides decreased Cu–O–Cu angle that generally leads to ferromagnetic coupling, a large hinge distortion of Cu$_2$O$_2$ core renders two NOCuOO coordination planes strongly tilted to each other. In the extreme case, with the dihedral angle between the two NOCuOO planes attaining $90^\circ$, the antiferromagnetic pathway via superexchange vanishes completely, which should lead to very strong ferromagnetic coupling (Figure 13). In our case, significantly tilted NOCuOO coordination planes at 76.6 and $81.0^\circ$ lead to relatively strong ferromagnetic coupling in 4 and 5, respectively. Thus, both structural parameters: small Cu-O-Cu angle and large Cu-O-Cu-O torsion angle in bis(phenoxido)dicopper(II) complexes, are indicative for ferromagnetic coupling, which is in agreement with previous correlations.\textsuperscript{14a}

CONCLUSIONS
We have reported the synthesis and systematic variation of exchange coupling constant ($J$) in a series of bis-($\mu$-phenoxido)dicopper(II) complexes 1 – 5 featuring tetradentate aminodiphenol H$_2$L$^{R1,R2,R3}$ ligands in which the ligands contain the same [O,N,N,O]-donor atoms but differ in substituents at phenol rings ($R1$, $R2$) and at an amine nitrogen atom ($R3$). The substituents are changed from methyl to tert-butyl on the phenol rings and from methyl to iso-propyl at the amine nitrogen atom, thus exerting different steric pressures on the participating copper centers. Among the substituents, $R1$ and $R2$ play a crucial role in controlling the Cu-O-Cu angle, Cu...Cu separation, and Cu-O-Cu-O torsion angle, whereas $R3$ controls the geometry around copper ions, changing from square pyramidal to square planar. Due to the fine tuning of structural parameters via ligand substituents, complexes 1 – 3 exhibit antiferromagnetic coupling, whereas 4 and 5 reveals ferromagnetic exchange. Thus, the average Cu-O-Cu bond angle, Cu-O-Cu-O torsion angle, and Cu...Cu separation are varied gradually within 1 – 5 series in the range 98.6 – 83.3°, 26.0 – 46.5°, and 2.982 – 2.633 Å, respectively. As a result, spin coupling changes gradually from strong antiferromagnetic ($J = -395$ cm$^{-1}$) to moderate ferromagnetic ($J = +53.2$ cm$^{-1}$) values. The crossover point at which the magnetic coupling is changed ($J = 0$) is determined at ca. 87°. Interestingly, 5 has the lowest Cu...Cu separation (2.633 Å) and smallest Cu-O-Cu bond angle (83.3°) and consequently a large ferromagnetic coupling constant ($J = +53.2$ cm$^{-1}$) reported thus far for bis($\mu$-phenoxido)dicopper(II) complexes. The results of DFT calculations are in agreement with the experimentally determined crossover angle and disclose excellent magneto-structural correlations in the series 1 – 5.
ASSOCIATED CONTENT

Supporting Information

Partially labelled POV-Ray diagram showing the atom labelling scheme in complexes 1 and 5 (Figures S1, S2), Cu···Cu Separation (Å) vs Coupling constant (J) plot (Figure S3), Cu–O–Cu–O Torsion Angle (°) vs Coupling constant (J) plot (Figure S4), Linear correlation between Cu-O-Cu angle and Cu-O-Cu-O torsion angle for non-planar bis(phenoxido)dicopper complexes (Figure S5), Spin density map for 2; a broken symmetry state obtained from B3LYP calculations (Figure S6), Spin density map for 3; a broken symmetry state obtained from B3LYP calculations (Figure S7, Spin density map for 4; a triplet state obtained from B3LYP calculations (Figure S8).

Accession Codes

CCDC 1859903-1859907 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Table 1. Summary of the Crystallographic Data for the Dicopper(II) Complexes 1 – 5.

| Parameters                     | 1                      | 2                      | 3                      | 4                      | 5                      |
|--------------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Composition                    | C$_{44}$H$_{60}$N$_{4}$O$_{4}$Cu$_{2}$ | C$_{49}$H$_{70}$Cl$_{2}$N$_{4}$O$_{4}$Cu$_{2}$ | C$_{68}$H$_{108}$N$_{4}$O$_{4}$Cu$_{2}$ | C$_{64}$H$_{100}$N$_{4}$O$_{4}$Cu$_{2}$ | C$_{76}$H$_{124}$N$_{4}$O$_{4}$Cu$_{2}$ |
| Formula wt.                    | 836.04                 | 976.06                 | 1204.66                | 1116.55                | 1300.86                |
| Crystal System                 | orthorhombic           | Triclinic              | monoclinic             | triclinic              | Monoclinic             |
| Space group                    | Pnna                   | P - I                  | P 2$_1$/c              | P - I                  | C 2/c                  |
| a, Å                           | 14.278(4)              | 12.6394(7)             | 15.660(2)              | 13.3104(13)            | 41.334(3)              |
| b, Å                           | 23.385(6)              | 13.0315(8)             | 25.044(3)              | 14.6501(13)            | 13.8244(9)             |
| c, Å                           | 12.942(4)              | 15.7942(9)             | 17.802(3)              | 17.9756(16)            | 29.215(2)              |
| a, deg                         | 90                     | 93.946(10)             | 90                     | 72.847(2)              | 90                     |
| β, deg                         | 90                     | 102.586(10)            | 103.149(5)             | 71.4641(18)            | 114.807(2)             |
| γ, deg                         | 90                     | 103.539(10)            | 90                     | 71.9747(18)            | 90                     |
| V, Å$^3$                       | 4321(2)                | 2448.6(2)              | 6798.6(16)             | 3084.3(5)              | 15153.5(18)            |
| $\rho_{\text{calc}}$, Mg m$^{-3}$ | 1.285                  | 1.324                  | 1.177                  | 1.202                  | 1.140                  |
| Temp, K                        | 150(2)                 | 293(2)                 | 150(2)                 | 150(2)                 | 150(2)                 |
| $\lambda$ (Mo K$_\alpha$), Å  | 0.71073                | 0.71073                | 0.71073                | 0.71073                | 0.71073                |
| Z                              | 4                      | 2                      | 4                      | 2                      | 8                      |
| $2\theta_{\text{max}}$ [°]    | 46.22                  | 61.858                 | 50.00                  | 59.27                  | 50.396                 |
| Reflections                    | 30428/                 | 27395/                 | 51815/                 | 34826/                 | 71312/                 |
| Collected/Unique               | 3020                   | 11729                  | 11963                  | 14517                  | 13580                  |
| $F(000)/\mu$ mm$^{-1}$        | 1768/ 1.029            | 1030/ 1.024            | 2600/ 2.024            | 1204/ 0.737            | 5648/ 0.610            |
| $R_{int}$/ GOF on $F^2$        | 0.1263/                | 0.0230/                | 0.1610/                | 0.0259/                | 0.0568/                |
|                                | 1.243                  | 1.273                  | 0.963                  | 1.033                  | 1.316                  |
| No. of parameters              | 250                    | 562                    | 745                    | 691                    | 865                    |
| $R1^a(F_0)$, wR2$^b$(F_0) (all data) | 0.0565, 0.0504, 0.0651, 0.0386, 0.0605, 0.1789 | 0.1542, 0.1699, 0.1487, 0.1280, 0.1789 | 0.0565, 0.0504, 0.0651, 0.0386, 0.0605, 0.1789 |
| Largest diff. peak, eÅ$^{-3}$  | 0.366, 0.983, 0.945, 0.565, 1.187 | -6.75, -0.787, -0.719, -0.469, -0.676 |
| Deepest hole, eÅ$^{-3}$        | -6.75                  | -0.787                 | -0.719                 | -0.469                 | -0.676                 |

$^a R = \frac{\sum||F_o|| - |F_c||}{\sum|F_o|}$. $^b$ wR = $[\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)]^{1/2}$.
Table 2. Selected Bond Distances (Å) and Angles (°) for 1 – 5.

| Parameters          | 1    | 2    | 3    | 4    | 5    |
|---------------------|------|------|------|------|------|
| Bond Distances (Å)  |      |      |      |      |      |
| Cu1-O1              | 1.878(4) | 1.865(2) | 1.860(4) | 1.8540(12) | 1.856(3) |
| Cu1-O2              | 1.979(4) | 2.008(18) | 1.976(3) | 2.0270(12) | 2.022(2) |
| Cu1-O3              | 1.954(4) | 1.9593(19) | 1.928(3) | 1.9175(12) | 1.941(2) |
| Cu1-N1              | 2.046(5) | 2.056(2) | 2.028(4) | 2.0294(15) | 2.024(3) |
| Cu1-N2              | 2.392(5) | 2.504(3) | -      | -      | -     |
| Cu2-O2              | 1.954(4) | 1.9428(19) | 1.914(3) | 1.9278(12) | 1.955(2) |
| Cu2-O3              | 1.979(4) | 2.0310(18) | 1.993(4) | 2.0323(13) | 2.006(2) |
| Cu2-O4              | 1.878(4) | 1.882(2) | 1.853(3) | 1.8535(12) | 1.866(2) |
| Cu2-N3              | 2.046(5) | 2.072(2) | 2.031(4) | 2.0296(15) | 2.008(3) |
| Cu2-N4              | 2.392(5) | 2.431(2) | -      | -      | -     |

| Bond Angles (°)     |      |      |      |      |      |
|---------------------|------|------|------|------|------|
| O1-Cu1-O3           | 165.15(18) | 162.94(9) | 168.16(15) | 168.10(5) | 167.21(10) |
| O1-Cu1-O2           | 91.05(18) | 89.14(8) | 92.65(3) | 94.92(5) | 93.25(10) |
| O3-Cu1-O2           | 75.32(19) | 75.68(8) | 75.51(14) | 75.20(5) | 74.21(9) |
| O1-Cu1-N1           | 95.98(19) | 96.04(9) | 97.26(16) | 97.61(6) | 97.68(11) |
| O3-Cu1-N1           | 93.44(18) | 94.61(9) | 94.35(16) | 94.17(5) | 93.57(11) |
| O2-Cu1-N1           | 151.36(19) | 154.75(9) | 165.43(14) | 151.95(6) | 159.49(11) |
| O1-Cu1-N2           | 97.0(2) | 99.22(10) | -      | -      | -     |
| O3-Cu1-N2           | 95.69(19) | 95.67(8) | -      | -      | -     |
| O2-Cu1-N2           | 124.61(19) | 123.28(8) | -      | -      | -     |
| N1-Cu1-N2           | 82.1(2) | 80.35(9) | -      | -      | -     |
| O4-Cu2-O2           | -     | 165.31(9) | 168.51(15) | 168.06(6) | 168.49(10) |
| O4-Cu2-O3           | -     | 90.14(8) | 93.15(15) | 94.55(5) | 94.23(10) |
| O2-Cu2-O3           | -     | 75.34(8) | 75.40(14) | 74.86(5) | 74.26(9) |
| O4-Cu2-N3           | -     | 95.42(9) | 96.65(16) | 97.45(6) | 97.23(12) |
| O2-Cu2-N3           | -     | 95.15(8) | 94.76(15) | 94.49(5) | 93.52(11) |
| O3-Cu2-N3           | -     | 144.11(8) | 170.02(15) | 152.17(5) | 157.36(11) |
| O4-Cu2-N4           | -     | 99.81(9) | -      | -      | -     |
| O2-Cu2-N4           | -     | 91.95(8) | -      | -      | -     |
| O3-Cu2-N4           | -     | 133.35(8) | -      | -      | -     |
| N3-Cu2-N4           | -     | 80.55(8) | -      | -      | -     |

Table 3. Cu-O-Cu Bond Angle, Cu···Cu Separation and Hinge Distortion of the Cu₂O₂ Framework in the Complexes 1 – 5.

| Complexes | Cu1-O2-Cu2 Angle (°) | Cu1-O3-Cu2 Angle (°) | Average Cu-O-Cu Angle (°) | Cu···Cu Separation (Å) | Phenyl conf. | Cu–O–Cu–O Torsion Angle (°) |
|-----------|---------------------|---------------------|--------------------------|------------------------|--------------|-----------------------------|
|           |                     |                     |                          |                        |              |                             |
Table 4. Electronic Spectral Data from the Complexes 1 – 5.

| Compounds                                                                 | λ, nm (ε, L mol⁻¹ cm⁻¹)     |
|---------------------------------------------------------------------------|------------------------------|
| [Cu₂(L⁺⁻)(L⁻⁻)] (1) (1)                                                   | 412 (5080), 473 (3916), 640 (880) |
| [Cu₂(L⁺⁻)(L⁻⁻)]·CH₂Cl₂ (2)                                               | 410 (4880), 474 (3600), 636 (990). |
| [Cu₂(L⁺⁻)(L⁻⁻)]·2H₂O (3)                                                 | 426 (6800), 634 (1500), 775 (1060) |
| [Cu₂(L⁺⁻)(L⁻⁻)] (4)                                                     | 435 (5430), 658 (1250), 830 (630) |
| [Cu₂(L⁺⁻)(L⁻⁻)]·H₂O (5)                                                  | 434(5280), 533(2480), 661(1400), 840(872) |

Table 5. Structural and Magnetic Fit Parameters for Complexes 1 – 5.

| Complexes | Average Cu-O-Cu Angle (°) | Cu···Cu Distance (Å) | J (cm⁻¹)   | g          | zJ(cm⁻¹)          | TIP (cm³.mol⁻¹) |
|-----------|---------------------------|----------------------|------------|------------|-------------------|----------------|
| 1         | 98.63                     | 2.9822(16)           | −395.1 ± 0.6 | 2.237 ± 0.005 | -                 | -              |
| 2         | 97.92                     | 2.9927(4)            | −259.4 ± 0.8 | 1.784 ± 0.006 | -2.0 ± 0.8         | (4.2 ± 0.08) × 10⁻³ |
| 3         | 94.39                     | 2.8730(2)            | −185.4 ± 0.4 | 2.242 ± 0.002 | -                 | -              |
| 4         | 86.95                     | 2.7205(4)            | +46 ± 2     | 2.122 ± 0.004 | -0.009 ± 0.007    | -              |
| 5         | 83.27                     | 2.6327(6)            | +53.2 ± 0.4 | 2.0390 ± 0.0009 | -0.030 ± 0.002   | -              |

Table 6. Calculated and Experimentally Determined Exchange Coupling Constants [J, cm⁻¹].

| Complexes | calc. | exp.    |
|-----------|-------|---------|
| 1         | −323  | −395.1 ± 0.6 |
| 2         | −249  | −259.4 ± 0.8 |
|   |   |   |
|---|---|---|
| 3 | –190 | –185.4 ± 0.4 |
| 4 | +22.3 | +46 ± 2 |
| 5 | +28.6 | +53.2 ± 0.4 |

**Scheme 1.** Synthesis of iminodiphenol ligands.

**Scheme 2.** Synthetic scheme for bis(µ-phenoxido)dicopper(II) complexes 1 – 5.
R1 = Me, R2 = Me, R3 = Me (1)
R1 = Me, R2 = Me, R3 = Et (2)
R1 = i-Pr, R2 = i-Pr, R3 = i-Pr (3)
R1 = t-Bu, R2 = Me, R3 = i-Pr (4)
R1 = t-Bu, R2 = t-Bu, R3 = i-Pr (5)
Figure 1. Partially labeled POV-Ray (in ball and stick form) diagram showing the atom labeling scheme in complex 2. Hydrogen atoms are omitted for clarity.
Figure 2. (a) Partially labeled POV-Ray (in ball and stick form) diagram showing the atom labeling scheme for complex 3; hydrogen atoms are omitted for clarity. (b) Dihedral angle between the two basal planes around the copper centers.

Figure 3. Partially labelled POV-Ray (in ball and stick form) diagram showing the atom labelling scheme in complex 4. Hydrogen atoms are omitted for clarity.
Figure 4. Uv-Vis spectra of complexes 1 – 5 recorded in dichloromethane.

Figure 5. Temperature dependence of $\chi T$ for compounds 1 – 5 measured under a 1000 Oe dc field. Solid lines correspond to the fit using PHI.
Figure 6. Field dependence of the magnetization at 1.8 K for compounds 4 and 5. The solid lines correspond to the fit.

Figure 7. Correlation between experimentally determined exchange coupling constant $J$ and Cu-O-Cu angle in 1 – 5.
Figure 8. Correlation between calculated exchange coupling constant $J$ and Cu-O-Cu angle in 1–5.

Figure 9. Correlation between calculated exchange coupling constant $J$ and Cu–O–Cu–O torsion angle in 1–5.
Figure 10. Correlation between Cu-O-Cu angle and Cu-O-Cu-O torsion angle in 1 – 5.

Figure 11. Spin density map for 1; a broken symmetry state obtained from B3LYP calculations is shown.
Figure 12. Spin density map for 4; a triplet state obtained from B3LYP calculations.

Figure 13. Spin density maps for 1 (left) and 5 (right) revealing more coplanar and more orthogonal arrangement of magnetic orbitals, respectively.
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