

Bi- and Trinuclear Copper(II) Complexes of a Sterically Constrained Phenol-Based Tetradentate Ligand: Syntheses, Structures, and Magnetic Studies

Suman Mukhopadhyay,[†] Debdas Mandal,[†] Pabitra Baran Chatterjee,[†] Cédric Desplanches,[‡] Jean-Pascal Sutter,^{*‡} Ray J. Butcher,[§] and Muktimoy Chaudhury^{*†}

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700 032, India, Institut de Chimie de la Matière Condensée de Bordeaux UPR 9048 CNRS, Université Bordeaux I, Avenue Dr. Schweitzer, F-33608 Pessac, France, and Department of Chemistry, Howard University, Washington, D.C. 20059

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Copper(II) complexes (**1–3**) of a sterically constrained phenol-based tetradentate N_2O_2 ligand 1,4-bis(2-hydroxy-3,5-dimethylbenzyl)piperazine (H_2L) have been reported. The associated anions of the copper(II) ion precursors have profound influence on the stoichiometry of the products. Thus, with perchlorate ion, the product is a binuclear compound $[Cu_2L_2]$ (**1**), while with coordinating anions viz. Cl^- and N_3^- , the products $[Cu_3L_2Cl_2(H_2O)] \cdot 1/2H_2L$ (**2**) and $[Cu_3L_2(N_3)_2(CH_3OH)] \cdot 4H_2O$ (**3**) have trigonular trinuclear composition. The syntheses, X-ray structures, and spectroscopic and magnetic properties of these complexes are described. Compound **1** has a noncentrosymmetric structure with a rectangular $Cu_2(OPh)_2$ core. It appears to be a rare example of a phenolato-bridged Cu(II) dimer exhibiting ferromagnetic interactions ($J = 0.93 \text{ cm}^{-1}$), a behavior in agreement with the theoretical predictions but seldom observed experimentally. In compounds **2** and **3**, the copper centers are triangularly disposed, and the molecules have a shape much like that of a butterfly. The terminal copper centers Cu(1) and Cu(2) in **2** and **3** have distorted square pyramidal geometry, connected to each other by a bridging chloro- (in **2**) or azido ligand (in **3**) in “end to end” fashion. The central copper center (Cu(3) in **2** and Cu in **3**) in both the compounds has distorted square planar geometry. The separations between the metal centers, viz. $Cu(1) \cdots Cu(2)$, $Cu(2) \cdots Cu(3)$, and $Cu(3) \cdots Cu(1)$, are 4.826, 3.214, and 3.244 Å, respectively, in **2**. The corresponding distances in **3** are 5.590, 3.178, and 3.485 Å, respectively. The overall magnetic behaviors in **2** and **3** are consistent with antiferromagnetic interactions between the spin centers. In **3**, the exchange couplings between the terminal and central copper centers $J_{Cu(1)-Cu}$ and $J_{Cu(2)-Cu}$ appear to be equal (-234 cm^{-1}), resulting in an $S = 1/2$ ground state at temperatures near or below 77 K.

Introduction

The chemistry of polynuclear copper complexes has become a fascinating area of research in contemporary coordination chemistry following the discovery of multicopper active sites in several blue copper oxidases^{1–4} and devel-

opment of novel functional materials showing molecular ferromagnetism⁵ and specific catalytic properties.⁶ In a few of these multicopper enzymes, it has been established by X-ray crystallography,⁷ MCD spectroscopy,⁸ and magnetic

* To whom correspondence should be addressed. E-mail: icmc@mahendra.iacs.res.in (M.C.); jpsutter@icmcb.u-bordeaux.fr (J.-P.S.).

[†] Indian Association for the Cultivation of Science.

[‡] Institut de Chimie de la Matière Condensée de Bordeaux.

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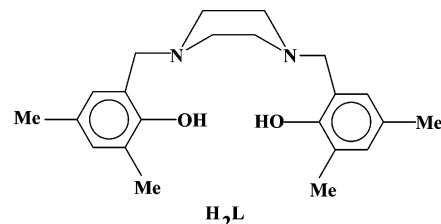
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studies⁹ that a trinuclear array of copper centers may be the essential functional unit of the cofactors which catalyze the $4e^-/4H^+$ reduction of dioxygen to water. The fully oxidized form of ascorbate oxidase has a triangular arrangement of Cu(II) atoms⁷ with Cu...Cu separations in the range 3.66–3.90 Å and bridged by hydroxo or oxo group. This has prompted several recent studies involving the syntheses of small molecule analogues of triangular copper biochromophores.^{10–16}

Apart from this biological significance, trinuclear triangular copper(II) centers also enjoy a clear fascination of the magnetochemists, as the complexes offer the opportunities to test magnetic exchange models on more complicated systems^{17–32} than the extensively studied binuclear types.³³ Many of these complexes have $[Cu_3(\mu-X)(\mu-L)_3]$ ($X = O^{2-}$,

OH^- , OCH_3^- , CO_3^{2-} and Cl^- , etc.) triangular core^{23–32} with L^- bridges, and they exhibit interesting magnetic properties. These studies offer opportunities to focus our attention on the properties of spin-quartet ground states in ferromagnetic exchange coupled systems or more complex behaviors due to, for instance, spin-frustrations.³⁴

Herein, we report the coordination chemistry of copper(II) with a sterically constrained phenol-based tetradentate N_2O_2 ligand viz. 1,4-bis(2-hydroxy-3,5-dimethyl-benzyl)-piperazine (H_2L). Two of the reported compounds have



triangular trinuclear composition with aesthetically pleasing butterfly type structures, while the remaining one has a binuclear $Cu_2(\mu-OPh)_2$ core. We provide here a rare example of phenolato-bridged dicopper(II) system with ferromagnetic interactions.

Experimental Section

Materials. Piperazine and 2,4-dimethylphenol were purchased from Aldrich. Solvents were reagent grade, dried by standard methods³⁵ and distilled under nitrogen prior to their use. All other reagents are available commercially and used as received.

Syntheses. Ligand. 1,4-Bis(2-hydroxy-3,5-dimethylbenzyl)-piperazine (H_2L). Piperazine (4.3 g, 50 mmol) was dissolved in methanol (50 mL), and 9.3 mL (135 mmol) of aqueous formaldehyde solution (40%) was added. A white precipitate sometimes appears at this point, which redissolves on heating. The mixture was refluxed for 2 h, and then, about 12.2 g (100 mmol) of 2,4-dimethylphenol, diluted with 60 mL of methanol, was added. The resulting solution was refluxed for 8 h when a white precipitate began to appear. Refluxing was continued further for ca. 4 h. The solution was then cooled to room temperature, and the product was collected by filtration and finally recrystallized from hot acetone. Yield: 9.0 g (51%). Mp: 184°C. Anal. Calcd for $C_{22}H_{30}N_2O_2$: C, 74.57; H, 8.47; N, 7.90. Found: C, 74.64; H, 8.47; N, 8.03%. IR (KBr disk, cm^{-1}): 2820, 1482, 1245, 1003. UV-vis (CH_2Cl_2), [λ_{max}/nm ($\epsilon_M/mol^{-1} cm^2$)]: 279 (14 700), 230 (8200). 1H NMR (300

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Table 1. Crystal Data, Data Collection, and Refinement Parameters for the Complexes **1**, **2**, and **3**

	1	2	3
formula	C ₄₄ H ₅₆ Cu ₂ N ₄ O ₄	C ₅₅ H ₇₃ Cl ₂ Cu ₃ N ₅ O ₆	C ₄₅ H ₆₈ Cu ₃ N ₁₀ O ₉
fw	832.01	1161.70	1082.71
T (K)	293	293	293
cryst size (mm ³)	0.54 × 0.48 × 0.23	0.34 × 0.29 × 0.18	0.45 × 0.40 × 0.15
cryst syst	monoclinic	rhombohedral	monoclinic
space group	P2 ₁ /n	R $\bar{3}$	P2 ₁ /c
a (Å)	14.618(3)	31.597(4)	12.273(3)
b (Å)	12.092(2)	31.597(4)	16.692(3)
c (Å)	23.066(5)	36.321(7)	24.414(5)
α (deg)	90	90	90
β (deg)	96.656(16)	90	94.996(4)
γ (deg)	90	120	90
V (Å ³)	4050.0(13)	31404(8)	4982.6(18)
Z	4	18	4
ρ _{calcd} (g cm ⁻³)	1.365	1.106	1.443
F(000)	1752	10926	2264
radiation used	Cu Kα	Mo Kα	Mo Kα
μ (mm ⁻¹)	1.663	1.024	1.332
no. indep reflns, total	5534	12409	11800
obsd [I ≥ 2σ(I)]	4487	3302	4687
no. params	551	476	621
R ₁ , wR ₂ (all data) ^a	0.1062, 0.2586	0.2364, 0.2230	0.2331, 0.2773
R ₁ , wR ₂ (obsd reflns)	0.0957, 0.2403	0.0670, 0.1725	0.0952, 0.2211
GOF	1.095	0.768	0.953

$$^a \text{wR}_2 = [\sum(w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}, R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \text{ and } S = [\sum(w(F_o^2 - F_c^2)^2) / (n - p)]^{1/2}.$$

MHz, CDCl₃, 25 °C), δ/ppm: 10.5 (br, 2H, phenolic OH), 6.86 (s, 2H, phenyl ring protons), 6.62 (s, 2H, phenyl ring protons), 3.65 (s, 4H, benzylic), 2.58 (br, 8H, piperazine ring protons), 2.20 (s, 12H, CH₃).

Complexes. [Cu₂(L)₂] (1**).** Copper(II) perchlorate hexahydrate (0.18 g, 0.5 mmol) was dissolved in 25 mL of methanol. It was added dropwise to a stirring suspension of ligand H₂L (0.18 g, 0.5 mmol) in 10 mL of methanol. A brown solution obtained at this stage was treated with 2 equiv of Et₃N (0.10 g, 1 mmol) with constant stirring when a green solution was obtained. It was refluxed for 1 h, cooled to room temperature, and filtered. The filtrate volume was reduced to ca. 15 mL by rotary evaporation and was kept at 4 °C for an overnight period to obtain a dark green crystalline compound along with crystals suitable for X-ray diffraction analysis. Yield: 0.11 g (55%). Anal. Calcd for C₄₄H₅₆Cu₂N₄O₄: C, 63.46; H, 6.73; N, 6.73. Found: C, 63.11; H, 6.77; N, 6.89%. IR (KBr disk, cm⁻¹): 2910, 2857, 1606, 1471, 1439, 1309, 1243, 1089, 996, 877, 797. UV-vis (CH₂Cl₂), [λ_{max}/nm (ε_M/mol⁻¹ cm²): 591 (sh), 432 (6650), 274 (27 200). μ_{eff}: 2.39 μ_B.

[Cu₃(L)₂Cl₂(H₂O)]·1/2H₂L (2**).** Ligand H₂L (0.18 g, 0.5 mmol) was taken in 15 mL of chloroform and neutralized with 2 equiv of Et₃N (0.10 g, 1 mmol). To the stirred ligand solution was then added copper(II) chloride dihydrate (0.09 g, 0.5 mmol) in 15 mL of methanol when a brown solution was obtained. It was stirred for another 30 min and then filtered. The filtrate was kept in a refrigerator for an overnight period to get a brown crystalline compound along with some X-ray diffraction quality crystals. It was filtered, washed with diethyl ether (2 × 5 mL), and dried in vacuo. Yield: 0.11 g (57%). Anal. Calcd for C₅₅H₇₃Cl₂Cu₃N₅O₆: C, 56.81; H, 6.28; N, 6.02. Found: C, 55.83; H, 6.77; N, 6.05%. IR (KBr disk, cm⁻¹): 3447, 3356, 1608, 1485, 1302, 1242, 1161, 1121. UV-vis (CH₂Cl₂), [λ_{max}/nm (ε_M/mol⁻¹ cm²): 716 (sh), 438 (5000), 279 (17 800). μ_{eff}: 2.02 μ_B.

[Cu₃(L)₂(N₃)₂(CH₃OH)]·4H₂O (3**).** About 0.18 g (0.5 mmol) of H₂L was dissolved in dichloromethane (15 mL). A methanolic solution (10 mL) of Cu(ClO₄)₂·6H₂O (0.18 g, 0.5 mmol) was added dropwise to obtain a brown solution. Et₃N (2 equiv, 0.10 g, 1 mmol) was then added to this solution with stirring followed by the addition of sodium azide (0.03 g, 0.5 mmol) in solid. The solution was stirred

for another 1 h, concentrated by rotary evaporation to ca. 10 mL volume, and filtered. The filtrate upon standing overnight in a refrigerator (4 °C) yielded a brown crystalline compound along with X-ray diffraction quality crystals. Yield: 0.11 g (60%). Anal. Calcd for C₄₅H₆₈Cu₃N₁₀O₉: C, 49.87; H, 6.28; N, 12.93. Found: C, 50.38; H, 6.39; N, 12.52%. IR (KBr disk, cm⁻¹): 3443, 2915, 2051, 1613, 1471, 1305, 1244, 1157, 1087, 862, 798. UV-vis (CH₂Cl₂), [λ_{max}/nm (ε_M/mol⁻¹ cm²): 428 (6500), 276 (15 900). μ_{eff}: 2.19 μ_B.

Physical Measurements. The IR and UV-vis spectra and elemental analyses were done using the same instrumentation facilities as described elsewhere.^{36,37} Magnetic susceptibility and magnetization experiments on powdered polycrystalline samples were performed on a Quantum Design MPMS-5S SQUID magnetometer under an applied magnetic field of 5000 Oe in the temperature range 2–300 K. The data were corrected for the diamagnetic contributions using Pascal's constants. A JEOL-JES RE 3X machine combined with an ESPRIT 330 data processing system was used to record the X-band EPR spectra at room temperature as well as in the frozen state.

X-ray Crystallography. Intensity data for the blue crystal of **1** (0.54 × 0.48 × 0.23 mm³) were collected at room temperature on a Siemens P4 four-circle diffractometer using the θ–2θ technique, while for the dark crystals of **2** (0.34 × 0.29 × 0.18 mm³) and **3** (0.45 × 0.40 × 0.15 mm³), intensity data were collected on a Bruker 1K SMART CCD diffractometer, the former diffractometer using graphite-monochromated Cu Kα X-radiation (λ = 1.541 78 Å) and the latter, graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystallographic parameters and residuals are given in Table 1. No crystal decay was observed during the data collections. The structures were solved by direct methods using SHELXS-97 package³⁸ of software. Final refinements were done by a full-matrix least-squares procedure³⁹ based on all data minimizing wR₂ =

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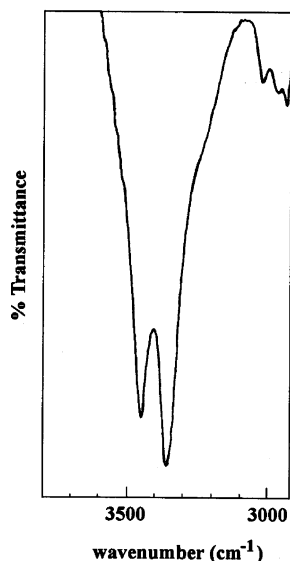


Figure 1. Relevant region (3700–3000 cm^{-1}) in the IR spectrum (in KBr disk) of **2**, showing the split in the $\nu(\text{O–H})$ stretching mode due to hydrogen bonded (asymmetric) aqua ligand.

$[\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)]^{1/2}$, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, and $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. All non-hydrogen atoms were refined as anisotropic, and the hydrogen atomic positions were fixed relative to the bonded carbons with isotropic thermal parameters fixed.

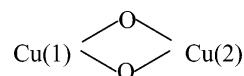
Results and Discussion

Synthesis. A sterically constrained tetradentate ligand (H_2L) has been used here to prepare bi- and trinuclear Cu(II) complexes. The reactions are anion dependent. With copper(II) perchlorate hexahydrate, the product obtained is a phenoxy-bridged binuclear compound (**1**) that allows both the metal centers to have square pyramidal geometry. On the other hand, a precursor with a coordinating anion (viz. chloride ion) generates a trinuclear product **2** with an aesthetically pleasing butterfly type structure. As revealed from X-ray crystallography (see later), one of the phenoxy oxygen atoms of the tetradentate (L)²⁻ ligand as well as a chloride ligand are acting as bridge between the copper ion centers to build the trinuclear framework in **2**. When chloride is replaced by a pseudohalide ion viz. N_3^- , the product is **3** with a closely comparable trinuclear structure involving a bridging (“end to end”) and a monodentate N_3^- ligand. As revealed from the elemental analysis, **2** has 0.5 mol of free ligand associated per mole of the compound, an interesting observation, later confirmed by X-ray crystal structure analysis.

IR spectra of **1–3** display all the characteristic bands of the coordinated tetradentate ligand (L)²⁻. One prominent such band appears at ca. 1240 cm^{-1} due to $\nu(\text{C–O}/\text{phenolate})$ stretching vibrations. Of particular interest in the spectrum of **2** is the appearance of a sharp twin band in the high-frequency region at 3447 and 3356 cm^{-1} as displayed in Figure 1. We believe these bands originate from a coordinated water molecule, which remains hydrogen bonded to nearby donor (phenoxy) atom(s). This interpretation gains further ground from the X-ray crystallographic analysis of

2 (see later). Compound **3** also displays a very strong band at 2051 cm^{-1} due to asymmetric stretching vibrations of the coordinated azido group.⁴⁰

Description of Crystal Structures. The molecular structure of **1** is shown in Figure 2. Important interatomic parameters are listed in Table 2. The molecule has a noncentrosymmetric structure with a binuclear $\text{Cu}_2(\mu\text{-OPh})_2$ rectangular core. Each copper center is five-coordinated and exists in a geometry based on a square pyramid. The basal positions around Cu(1) are taken up by two tertiary nitrogen N(1A) and N(1B) and two phenolate oxygen atoms O(1A) and O(1B), all coming from a coordinated tetradentate (L)²⁻ ligand. Corresponding donor atoms around the Cu(2) center are N(1C), N(1D), O(1C), and O(1D), respectively, also coming exclusively from a second ligand molecule. One phenoxy oxygen atom from each ligand acts as a bridge between the copper centers. Thus O(1B) atom which occupies a basal position around Cu(1) also takes up the lone apical position of Cu(2) to complete the latter’s pentacoordination geometry. Similarly, Cu(1) utilizes O(1D) atom to occupy its apical position, thus completing the



rectangular core. The Cu(1)–O(1B)–Cu(2) and Cu(2)–O(1D)–Cu(1) angles are almost similar, 92.19(13)° and 92.55(12)°, respectively. The trans angles in the basal plane around Cu(1), O(1B)–Cu(1)–N(1A) and O(1A)–Cu(1)–N(1B), are 164.29(17)° and 160.80(16)°, respectively. The corresponding angles at Cu(2) are 164.61(16)° and 159.92(15)°, respectively. The Cu(1) atom is displaced by 0.2227 Å from its least squares basal plane (mean deviation 0.0513 Å) toward the apical O(1D) atom. Corresponding displacement of Cu(2) from its least-squares basal plane (mean deviation, 0.0758 Å) is 0.2217 Å. The Cu–N distances are almost identical, lying in the range 2.021(4)–2.039(4) Å. Cu–O distances, on the other hand, show interesting variations. While the basal distances Cu(1)–O(1A) and Cu(1)–O(1B), 1.894(3) Å and 1.935(3) Å, respectively, (corresponding distances at Cu(2) are 1.898(3) and 1.936(3) Å, respectively) are in the normal range, the apical Cu(1)–O(1D) distance 2.375(3) Å (2.387(3) Å) is by far the longest as expected for an axially elongated geometry with a Jahn–Teller ion. The Cu(1)···Cu(2) separation is 3.130 Å in this molecule.

The molecular structures of the trinuclear complexes **2** and **3** are displayed in Figures 3 and 4, respectively, and their metrical parameters in Tables 3 and 4, respectively. Both are noncentrosymmetric molecules and appear to have an appearance like a butterfly. The terminal copper atoms Cu(1) and Cu(2) in both molecules have square pyramidal geometry. The basal positions are taken up by two tertiary nitrogen and two phenoxy oxygen atoms, all coming from a tetradentate (L)²⁻ ligand. In **2**, the apical positions of Cu(1) and Cu(2) are taken up by a bridging chloride ion while in

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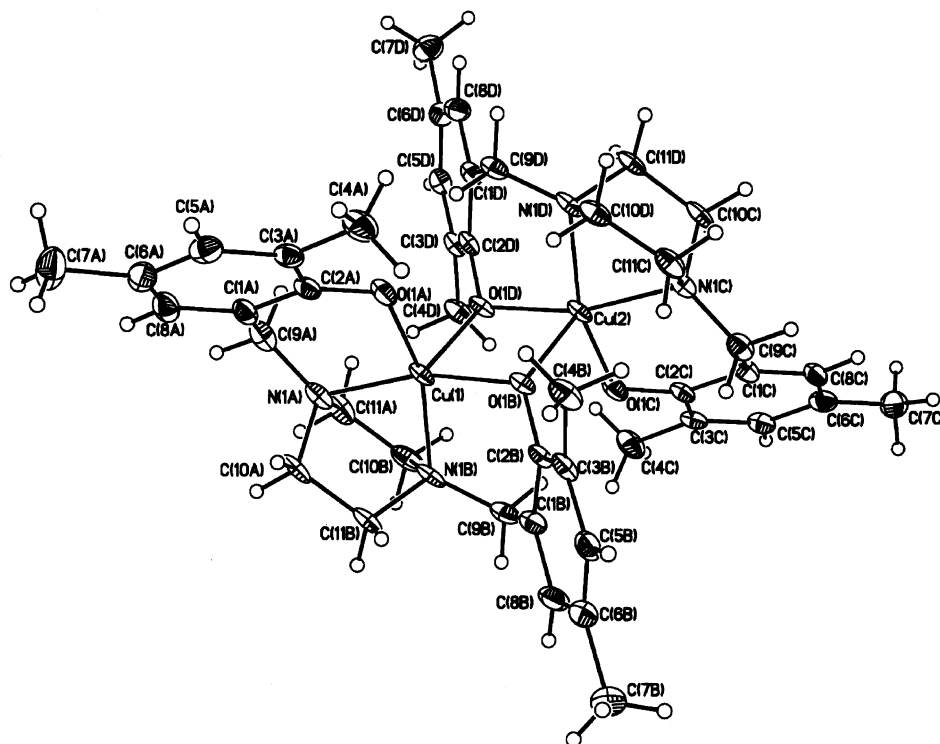


Figure 2. Molecular structure of $[\text{Cu}_2(\text{L})_2]$ (**1**) showing the atom-numbering scheme.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**

Bond Lengths			
Cu(1)–O(1A)	1.894(3)	Cu(2)–O(1C)	1.898(3)
Cu(1)–N(1B)	2.025(4)	Cu(2)–N(1C)	2.021(4)
Cu(1)–O(1D)	2.375(3)	Cu(2)–O(1B)	2.387(3)
Cu(1)–O(1B)	1.935(3)	Cu(2)–O(1D)	1.936(3)
Cu(1)–N(1A)	2.037(4)	Cu(2)–N(1D)	2.039(4)
Bond Angles			
Cu(1)–O(1B)–Cu(2)	92.19(13)	Cu(2)–O(1D)–Cu(1)	92.55(12)
O(1A)–Cu(1)–O(1B)	95.56(15)	O(1C)–Cu(2)–O(1D)	96.01(15)
O(1B)–Cu(1)–N(1B)	93.36(16)	O(1D)–Cu(2)–N(1D)	92.57(15)
O(1B)–Cu(1)–N(1A)	164.29(17)	O(1D)–Cu(2)–N(1C)	164.61(16)
O(1A)–Cu(1)–O(1D)	102.29(14)	O(1C)–Cu(2)–O(1B)	101.41(14)
N(1B)–Cu(1)–O(1D)	95.00(14)	N(1D)–Cu(2)–O(1B)	97.08(13)
O(1A)–Cu(1)–N(1B)	160.80(16)	O(1C)–Cu(2)–N(1D)	159.92(15)
O(1A)–Cu(1)–N(1A)	95.07(17)	O(1C)–Cu(2)–N(1C)	95.36(16)
N(1B)–Cu(1)–N(1A)	73.20(19)	N(1C)–Cu(2)–N(1D)	73.46(17)
O(1B)–Cu(1)–O(1D)	87.80(12)	O(1D)–Cu(2)–O(1B)	87.41(12)
N(1A)–Cu(1)–O(1D)	101.20(14)	N(1C)–Cu(2)–O(1B)	100.46(14)

3, it is a bridging (“end to end”) N_3^- ion that completes the pentacoordination geometry. The Cu(1)–Cl and Cu(2)–Cl distances are 2.655(2) and 2.652(2) Å, respectively, and the included angle Cu(1)–Cl–Cu(2) is 130.81(9)°. The Cu(1) atom is displaced from the least squares basal plane (mean deviation 0.0448 Å) by 0.2082 Å toward the apical Cl atom. Corresponding displacement of Cu(2) is 0.2195 Å. In **3**, the Cu(1)–N(11) and Cu(2)–N(13) distances are 2.280(9) and 2.295(8) Å, respectively. The Cu(1) atom is displaced from its least-squares basal plane (mean deviation 0.0491 Å) by 0.2315 Å toward the apical azido ligand. Corresponding displacement of Cu(2) from its basal plane (mean deviation 0.0221 Å) is 0.2308 Å.

Besides these terminal copper centers, there is a central copper atom in these molecules viz. Cu(3) in **2** and Cu in **3**. Both these central copper atoms have distorted square planar

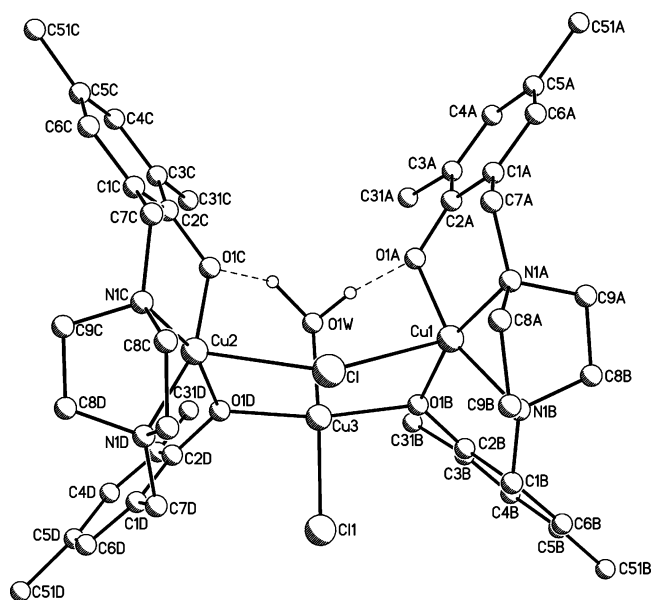


Figure 3. Molecular structure of the trinuclear complex **2** with atom-numbering scheme. The hydrogen atoms and the free ligand present have been omitted for clarity.

geometry. In **2**, four coordination sites of Cu(3) are taken up by two bridging phenoxo oxygen atoms O(1D) and O(1B), a coordinated aqua oxygen atom O(1W), and a chloro ligand Cl(1). In **3**, besides the bridging phenoxo ligands, the remaining two coordination sites of the central copper atom are taken up by a coordinated methanol oxygen O(1M) and a monodentate N_3^- ligand. The trans angles O(1D)–Cu(3)–O(1B) and O(1W)–Cu(3)–Cl(1) in **2** are 165.0(2)° and 157.16(17)°, respectively, and the Cu(3) atom is displaced from the mean plane (mean deviation, 0.3003 Å) by 0.1107 Å. Corresponding angles O(1D)–Cu–O(1A) and O(1M)–

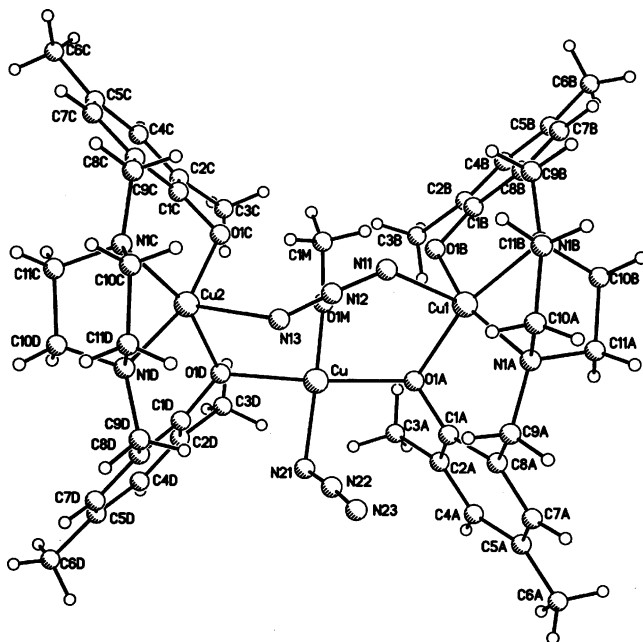


Figure 4. Molecular structure and atom-numbering scheme for the trinuclear complex **3**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **2**

Bond Lengths			
Cu(1)–O(1A)	1.914(5)	Cu(2)–O(1C)	1.873(6)
Cu(1)–N(1B)	2.000(6)	Cu(2)–N(1C)	2.017(8)
Cu(1)–O(1B)	1.964(5)	Cu(2)–O(1D)	1.943(5)
Cu(1)–N(1A)	2.001(6)	Cu(2)–N(1D)	2.035(8)
Cu(1)–Cl	2.655(2)	Cu(2)–Cl	2.652(2)
Cu(3)–O(1D)	1.951(5)	Cu(3)–O(1B)	1.959(5)
Cu(3)–O(1W)	1.982(5)	Cu(3)–Cl(1)	2.212(3)
Bond Angles			
O(1A)–Cu(1)–O(1B)	95.9(2)	O(1C)–Cu(2)–O(1D)	95.2(2)
O(1B)–Cu(1)–N(1B)	93.7(2)	O(1D)–Cu(2)–N(1D)	91.7(3)
O(1B)–Cu(1)–N(1A)	165.2(2)	O(1D)–Cu(2)–N(1C)	164.7(3)
O(1A)–Cu(1)–N(1B)	161.5(2)	O(1C)–Cu(2)–N(1D)	162.1(3)
O(1A)–Cu(1)–N(1A)	94.1(2)	O(1C)–Cu(2)–N(1C)	94.9(4)
N(1B)–Cu(1)–N(1A)	73.8(3)	N(1C)–Cu(2)–N(1D)	75.5(4)
O(1A)–Cu(1)–Cl	96.66(16)	O(1C)–Cu(2)–Cl	98.69(19)
N(1B)–Cu(1)–Cl	99.74(18)	N(1D)–Cu(2)–Cl	98.1(2)
O(1B)–Cu(1)–Cl	86.01(15)	O(1D)–Cu(2)–Cl	87.79(16)
N(1A)–Cu(1)–Cl	103.61(17)	N(1C)–Cu(2)–Cl	102.1(2)
O(1D)–Cu(3)–O(1B)	165.0(2)	O(1W)–Cu(3)–Cl(1)	157.16(17)
O(1D)–Cu(3)–O(1W)	85.7(2)	O(1B)–Cu(3)–O(1W)	87.1(2)
O(1D)–Cu(3)–Cl(1)	95.31(17)	O(1B)–Cu(3)–Cl(1)	96.37(16)
Cu(2)–Cl–Cu(1)	130.81(9)		

Hydrogen Bonds

A	H	B	A···B	A–H	H···B	A–H···B
O(1W)	H(1W1)	O(1C)	2.710(7)	1.16	1.79	132.3
O(1W)	H(1W2)	O(1A)	2.621(7)	1.01	1.64	164.3

Cu–N(21) in **3** are 175.1(2)° and 171.3(3)°, respectively, and the Cu atom is displaced from its least-squares basal plane (mean deviation 0.0699 Å) by 0.0682 Å.

As displayed in Figures 3 and 4, the terminal copper atoms Cu(1) and Cu(2) with associated coordinated tetradentate ligand look like unfolded (spread out) umbrellas. Their attachment as wings from both sides to the central copper atom completes the shape of a butterfly. Three copper centers are disposed at the corners of an isosceles triangle with Cu(1)···Cu(2), Cu(2)···Cu(3), and Cu(3)···Cu(1) separations

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex **3**

Bond Lengths			
Cu(1)–O(1A)	1.967(6)	Cu(2)–O(1D)	1.966(6)
Cu(1)–N(1B)	2.025(7)	Cu(2)–N(1C)	2.003(7)
Cu(1)–O(1B)	1.910(6)	Cu(2)–O(1C)	1.929(5)
Cu(1)–N(1A)	2.043(7)	Cu(2)–N(1D)	2.020(6)
Cu(1)–N(11)	2.280(9)	Cu(2)–N(13)	2.295(8)
Cu–O(1D)	2.007(5)	Cu–O(1A)	2.007(5)
Cu–O(1M)	1.915(6)	Cu–N(21)	1.924(8)
Bond Angles			
O(1A)–Cu(1)–O(1B)	95.7(2)	O(1C)–Cu(2)–O(1D)	95.6(2)
O(1B)–Cu(1)–N(1B)	94.9(3)	O(1C)–Cu(2)–N(1C)	94.0(3)
O(1B)–Cu(1)–N(1A)	160.2(3)	O(1C)–Cu(2)–N(1D)	164.0(3)
O(1A)–Cu(1)–N(1B)	163.8(3)	O(1D)–Cu(2)–N(1C)	161.5(2)
O(1A)–Cu(1)–N(1A)	93.8(3)	O(1D)–Cu(2)–N(1D)	93.1(2)
N(1B)–Cu(1)–N(1A)	72.5(3)	N(1C)–Cu(2)–N(1D)	74.2(3)
O(1B)–Cu(1)–N(11)	96.1(3)	O(1C)–Cu(2)–N(13)	98.5(3)
O(1A)–Cu(1)–N(11)	95.4(3)	O(1D)–Cu(2)–N(13)	88.5(3)
N(1B)–Cu(1)–N(11)	95.6(3)	N(1C)–Cu(2)–N(13)	105.7(3)
N(1A)–Cu(1)–N(11)	100.3(3)	N(1D)–Cu(2)–N(13)	95.1(3)
O(1M)–Cu–N(21)	171.3(3)	O(1M)–Cu–O(1A)	88.5(2)
O(1M)–Cu–O(1D)	86.6(2)	N(21)–Cu–O(1A)	94.3(3)
N(21)–Cu–O(1D)	90.5(3)	O(1D)–Cu–O(1A)	175.1(2)

being 4.826, 3.214, and 3.244 Å, respectively, in **2**. Corresponding distances in **3** are 5.590, 3.178, and 3.485 Å, respectively.

Another important aspect in the structure of **2** is the asymmetric nature of its coordinated water molecule which forms the antenna of our imaginary butterfly as displayed in Figure 3. Hydrogen atoms of this water molecule are attached to the phenoxy oxygen atoms O(1A) and O(1C) by strong hydrogen bonding, details of which are summarized in Table 3. The O–H distances are 1.16 and 1.01 Å that account for the appearance of strong twin bands in the high-frequency region of the IR spectrum of **2** as displayed in Figure 1 (vide supra).

Electronic Spectra. The electronic spectra of **1–3** have been recorded in CH₂Cl₂ solutions, and the data are summarized in the Experimental Section. The binuclear complex **1** displays a single d–d absorption at 591 nm in the form of a shoulder, as expected for a Cu(II) center in square pyramidal geometry.⁴¹ Spectra of the trinuclear complexes **2** and **3** are dominated by an LMCT band in the near-UV region due to the PhO[−] → Cu(II) transition. It appears at 438 nm (ε, 5000 mol^{−1} cm²) in **2** and at 428 nm (ε, 6500 mol^{−1} cm²) in **3**. For the binuclear complex **1**, such an LMCT band is observed at 432 nm (ε, 6650 mol^{−1} cm²). Remaining band maxima appearing below 300 nm are due to ligand internal transitions.

Magnetic Properties and EPR. Variable-temperature magnetic susceptibility measurements for the compounds **1–3** were carried out in the temperature range 2–300 K. The plot of χ_MT versus T for the binuclear Cu(II) compound **1** is shown in Figure 5. The value of 0.85 cm³ K mol^{−1} for χ_MT at 300 K is in agreement with two S = 1/2 spin and a g parameter deviating from 2.00 as usually found for Cu(II) ions (vide infra). The χ_MT remains invariant down to 20 K, and below this temperature, it sharply increases to 0.97 cm³

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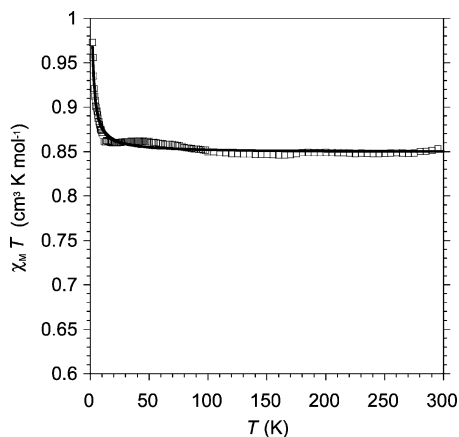


Figure 5. Experimental (□) and calculated (—) $\chi_{\text{M}}T$ versus T curve for compound **1**.

K mol^{-1} for 2 K revealing the occurrence of ferromagnetic interactions between the Cu(II) centers. These data have been analyzed with the Bleaney–Bowers⁴² equation, and the best fit to the experimental data leads to $g = 2.12$ and $J = 0.93 \text{ cm}^{-1}$ (agreement factor is 2×10^{-5}) confirming the existence of a weak ferromagnetic interaction between the Cu(II) centers. Whereas the agreement factor is rather good, a slight deviation between the calculated and experimental behavior is visible in the 100–20 K range. This could be ascribed to the contribution of small amounts of impurities such as Cu(II) as evidence by EPR (vide infra).

The observation of ferromagnetic interactions for a phenolato-bridged Cu(II) dimer is rather exceptional. Compound **1** belongs to the well documented family of derivatives for which two Cu(II) centers are linked through an oxygen atom of a ^-OR ligand ($\text{R} = \text{H, alkyl, phenyl}$).^{33b,43–49} These compounds are known to exhibit a magnetic behavior modulated by the Cu–O–Cu angle (θ); the interaction is ferromagnetic for angles close to 90° whereas it is antiferromagnetic for larger angles. The origin of this crossover is well understood. For a Cu(II) dimer, a theoretical description for the exchange interaction is given as $J = 2K_{\text{ab}} - [(\epsilon_{\text{g}} - \epsilon_{\text{u}})^2 / (J_{\text{aa}} - J_{\text{ab}})]$,⁵⁰ where K_{ab} stands for the exchange integral, ϵ_{g} and ϵ_{u} are the energies of the singly occupied molecular orbitals, and J_{aa} and J_{ab} are the one- and two-center Coulomb repulsion integrals. The first term of the expression corresponds to the ferromagnetic contribution to J whereas the second corresponds to the antiferromagnetic contribution. For θ values close to 90° , the energies of the two singly occupied

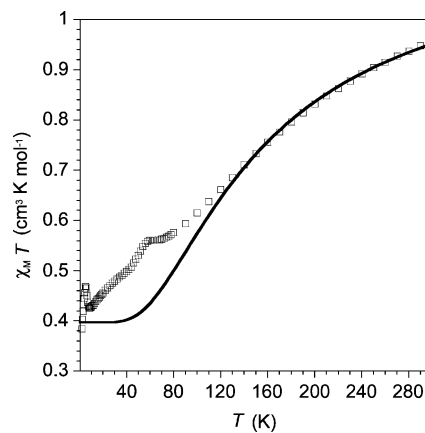


Figure 6. Experimental (□) and calculated (—) $\chi_{\text{M}}T$ versus T curve for compound **2**. The theoretical curve was calculated with the parameters deduced by fitting the experimental data in the 130–300 K range (see text).

molecular orbitals in the triplet state are very similar; consequently, the antiferromagnetic contribution may become so small that J is governed by the ferromagnetic term.^{33b,50,51} For the hydroxyl- and alkoxy-derivatives, the crossover from an antiferromagnetic to ferromagnetic behavior has been found to take place at angles around 97° . The phenolato derivatives are usually characterized by very strong antiferromagnetic interactions even for angles below 100° , and examples of ferromagnetic behavior are very rare.⁵² Moreover, the extrapolation of the linear relationship between J and θ , deduced from experimental data obtained from Schiff-base derivatives, suggests that ferromagnetic exchange should be found below the nonrealistic angle of 77° .⁴⁶ The discrepancy between the experimental law and the theoretical prediction was attributed to the existence of a possible alternative exchange pathway through the conjugated π -system of the Schiff-base ligand which may significantly contribute to the observed antiferromagnetic interaction.⁴⁶ Such an alternative pathway no longer exists for compound **1**, and the observed behavior can be confidently considered to be only mediated by the phenoxy-bridges. The ferromagnetic interaction between the two Cu(II) centers is thus in perfect agreement with the theoretical prediction. It should, however, be noticed that for compound **1** each bridging O-atom occupies an equatorial position in the coordination sphere of one Cu(II) whereas it is in axial position for the second, a situation which also leads to weak ferromagnetic exchange among the Cu centers.^{33b} Interestingly, our result also strongly supports the contribution of alternative exchange pathways in the magnetic behavior of Schiff-base derivatives.

In case of trinuclear Cu(II) complex **2**, the $\chi_{\text{M}}T$ versus T curve presents a rather intriguing behavior (Figure 6). The overall behavior is dominated by strong antiferromagnetic interactions between the spin carriers, but the curve presents a small “bump” at 58 K and a sharp and sudden peak at very low temperature. The organization of the three linked Cu(II) centers can be regarded as an isosceles triangle spin

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system with two equivalent exchange interactions occurring between the oxygen-bridged ions, Cu(1)–O(1B)–Cu(3) and Cu(3)–O(1D)–Cu(2), and one between the chlorine linked Cu(1) and Cu(2). Both should be antiferromagnetic, but the chlorine mediated exchange interaction is much weaker than the phenolato mediated interaction in compound **2** for which the geometrical features with Cu–O–Cu angles of 111.18° and 111.3° predict a strong exchange (discussion above). Therefore, the dominant antiferromagnetic behavior observed for compound **2** is attributed to the latter interactions. For the anomaly at 58 K, it has been carefully checked that this bump is not due to the presence of oxygen in the sample. The measurement has been repeated several times on two different batches of samples, and the trend is reproducible. It seems to us that a possible structural modification of the compound at temperatures near 60 K could be the origin of this behavior.^{53,54} The clear difference of slope of the $\chi_M T$ curve above and below this anomaly suggests that the structural rearrangement affects the geometry of the Cu–O–Cu connections. The origin of the behavior found below 10 K is more puzzling. An alternative or additional exchange pathway via the coordinated H₂O could be invoked. It has been shown that a H₂O unit leads to a ferromagnetic interaction when hydrogen bonded to two magnetic centers.⁵⁵ For compound **2**, this pathway would favor the parallel alignment of the moment located on Cu(1) and Cu(2) against the effect induced by the chlorine bridge. Considering that the structural data determined for compound **2** remain pertinent at least down to ca. 150 K, the magnetic behavior in the high-temperature range has been analyzed by a linear three spin model derived from the spin Hamiltonian $H = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3)$, the resulting expression for $\chi_M T$ is given by eq 1 where N stands for the Avogadro number, k for the Boltzmann constant, and β the Bohr magneton. Best fit of this expression to the experimental data in the temperature range 300–130 K yielded the exchange parameter $J = -121 \pm 2 \text{ cm}^{-1}$ and $g = 2.06$. In Figure 6, the calculated magnetic behavior has been plotted down to 2 K with these parameters.

$$\chi_M T = \frac{Ng^2\beta^2}{4k} \frac{10 + \exp\left(\frac{-3J}{2kT}\right) + \exp\left(\frac{-J}{2kT}\right)}{2 + \exp\left(\frac{-3J}{2kT}\right) + \exp\left(\frac{-J}{2kT}\right)} \quad (1)$$

The temperature dependence of $\chi_M T$ for complex **3** exhibits a rapid decrease reaching a plateau value of $0.43 \text{ cm}^3 \text{ K mol}^{-1}$ below 70 K (Figure 7). Such behavior indicates the occurrence of a strong antiferromagnetic interaction between the Cu(II) ions resulting in a ground state of $S = 1/2$. The spin system for compound **3** could also be regarded as an isosceles triangle. However, the structural data indicate that the bridging azido ligand is connected in apical position on both the Cu(II) centers. As a consequence, only a very weak

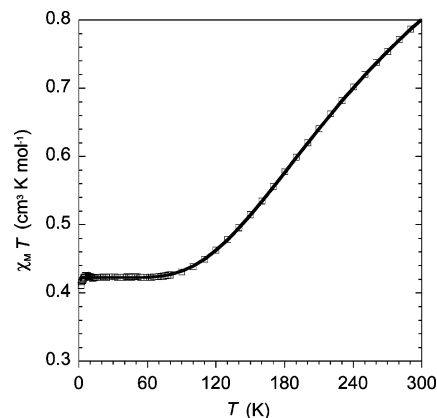
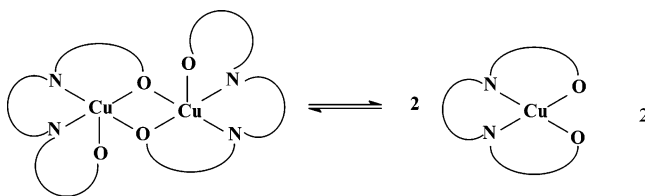


Figure 7. Experimental (□) and calculated (—) $\chi_M T$ versus T curve for compound **3**.

exchange interaction is anticipated through this link whereas strong antiferromagnetic interactions should be operative between the Cu ions bridged by the phenolato ligand. Therefore, the magnetic data have been analyzed by the linear three spin model given in eq 1. The best fit of this expression to the experimental curve (Figure 7) yielded the exchange parameter $J = -234 \text{ cm}^{-1}$ and $g = 2.12$ with an agreement factor of 10^{-5} . When compared to compound **2**, a much stronger exchange interaction is found for **3**. This might be ascribed to the well-documented incidence of the Cu–O–Cu angle (vide supra). Indeed, whereas this angle is of 111° for compound **2** with $J = -121 \text{ cm}^{-1}$ an average value of 114.3° is found for **3** with $J = -234 \text{ cm}^{-1}$. It can be noticed that the exchange parameters found for compounds **2** and **3** are much below those predicted for these angles by the relationship between J and θ for Schiff-base derivatives.⁴⁶ It has been reported that this relationship may also apply for phenolato-bridged linear trinuclear derivatives,⁵⁶ but not necessarily.⁵⁷

The X-band EPR spectrum of the binuclear complex **1** in CH₂Cl₂ solution (concentration $2.21 \times 10^{-3} \text{ M}$) is displayed in Figure 8. The spectrum reveals a well-resolved four-line pattern ($\langle g \rangle$, 2.098; $\langle A \rangle$, $84 \times 10^{-4} \text{ cm}^{-1}$) at room temperature, characteristic of an unpaired electron being coupled to a copper nuclear spin ($^{63,65}\text{Cu}$, $I = 3/2$). We believe the binuclear complex **1** dissociates to some extent in solution (eq 2), generating a mononuclear species, responsible for the four-line spectrum. Another alternative is the presence of a mononuclear impurity as established from magnetic studies (vide supra) that could give rise to the same behavior.



The trinuclear complexes **2** and **3** are EPR-silent at room temperature due to the persistence of moderately strong

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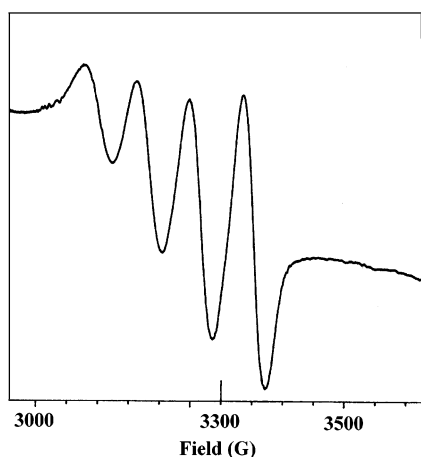


Figure 8. X-band EPR spectrum of **1** in CH_2Cl_2 solution at room temperature.

coupling as revealed from the susceptibility measurements. In frozen CH_2Cl_2 /toluene (1:1 v/v) solution, however, **3** displays well-resolved axial anisotropy at 77 K, corresponding to a single unpaired electron, giving g_{\parallel} and g_{\perp} values of 2.215 and 2.021, respectively, and $A_{\parallel} = 174 \times 10^{-4} \text{ cm}^{-1}$. The observed trend $g_{\parallel} > g_{\perp}$ indicates a $d_{x^2-y^2}$ -based ground state.¹⁷ The data correspond well with the results of magnetic susceptibility measurements on a powdered sample (vide supra) of **3**, revealing that the compound is essentially in an $S = 1/2$ ground state at temperatures near or below 77 K. Compound **2** is EPR-silent at 77 K as expected from the results of susceptibility measurements.

Concluding Remarks

A sterically constrained phenol-based tetradentate ligand H_2L has been used here to synthesize bi- and trinuclear copper(II) complexes. The nuclearity of the product depends

on the nature of the associated anion of the copper(II) ion precursor used during the synthesis. Thus, with a noncoordinating perchlorate anion, product **1** is a binuclear species, while with coordinating anion, viz. Cl^- or N_3^- , trinuclear chloro- and azido-bridged products **2** and **3**, respectively, are obtained in which the metal centers are triangularly disposed. In **2**, the separations between the metal centers are in the range 4.826–3.214 Å, quite in agreement with what is observed in the trinuclear active site of the oxidized form of ascorbate oxidase.⁷ In **3**, two of the three copper centers (Cu2 and Cu1) are widely separated (5.590 Å) due to the intervening “end-to-end” azido-bridge. Magnetic studies have revealed that compound **1** is a rare example of phenolato-bridged Cu(II) dimer exhibiting ferromagnetic interactions ($J = 0.93 \text{ cm}^{-1}$), a behavior in agreement with the theoretical predictions but seldom observed experimentally. For compounds **2** and **3** which display larger Cu–O–Cu angles, a moderately strong antiferromagnetic interaction ($J = -121$ and -234 cm^{-1} , respectively) was found. Whereas this results for **3** in an $S = 1/2$ ground state at temperatures near or below 77 K, with the ground state corroborated by the EPR spectrum in solution at 77 K, a sudden modification of the magnetic behavior has been observed for compound **2** below 100 K. For the latter compound, the deviation from the expected behavior for a triangular trinuclear spin system is ascribed to a structural rearrangement at low temperature.

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Supporting Information Available: X-ray crystallographic file in CIF format for compounds **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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