Inorganic Chemistry
Article
pubs.acs.org/IC

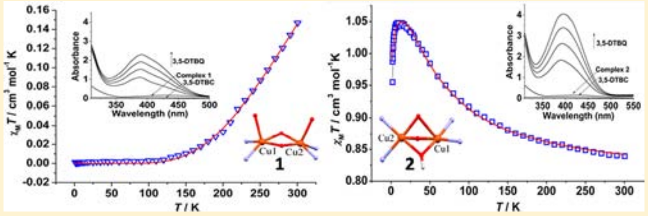
Insertion of a Hydroxido Bridge into a Diphenoxido Dinuclear Copper(II) Complex: Drastic Change of the Magnetic Property from Strong Antiferromagnetic to Ferromagnetic and Enhancement in the Catecholase Activity

Apurba Biswas,[†] Lakshmi Kanta Das,[†] Michael G. B. Drew,[‡] Carmen Diaz,[§] and Ashutosh Ghosh*[,†]

[†]Department of Chemistry, University College of Science, University of Calcutta, 92 APC Road, Kolkata 700 009, India
[‡]School of Chemistry, The University of Reading, P.O. Box 224, Whiteknights, Reading RG 66AD, U.K.
[§]Departament de Química Inorgànica, Universitat de Barcelona, Marti i Franques 1-11, 08028 Barcelona, Spain

Supporting Information

ABSTRACT: A diphenoxido-bridged dinuclear copper(II) complex, $[Cu_2L_2(ClO_4)_2]$ (**1**), has been synthesized using a tridentate reduced Schiff base ligand, 2-[[2-(diethylamino)-ethylamino]methyl]phenol (HL). The addition of triethylamine to the methanolic solution of this complex produced a novel triple bridged (double phenoxido and single hydroxido) dinuclear copper(II) complex, $[Cu_2L_2(OH)]ClO_4$ (**2**). Both complexes **1** and **2** were characterized by X-ray structural analyses, variable-temperature magnetic susceptibility measurements, and spectroscopic methods. In **1**, the two phenoxido bridges are equatorial–equatorial and the species shows strong antiferromagnetic coupling with $J = -615.6(6.1)$ cm^{-1}. The inclusion of the equatorial–equatorial hydroxido bridge in **2** changes the Cu···Cu distance from 3.018 Å (avg.) to 2.798 Å (avg.), the positions of the phenoxido bridges to axial–equatorial, and the magnetic coupling to ferromagnetic with $J = 50.1(1.4)$ cm^{-1}. Using 3,5-di-*tert*-butylcatechol as the substrate, the catecholase activity of the complexes has been studied in a methanol solution; compound **2** shows higher catecholase activity ($k_{cat} = 233.4$ h^{-1}) than compound **1** ($k_{cat} = 93.6$ h^{-1}). Both complexes generate identical species in solution, and they are interconvertible simply by changing the pH of their solutions. The higher catecholase activity of **2** seems to be due to the presence of the OH group, which increases the pH of its solution.



■ INTRODUCTION

Phenoxido/hydroxido-bridged dinuclear copper(II) complexes have received much attention for their interesting magnetic properties[1] as well as significant catecholase activities.[2] Their magnetic properties have been extensively studied in order to provide clear insight into the relationship between their structural features and the strength of the magnetic exchange interaction between the metal ions because copper(II) ions have an $S = {}^1/_2$ spin, which make them easier to deal with from a theoretical point of view. It is now well established that the exchange coupling of diphenoxido/hydroxido-bridged dinuclear copper(II) complexes containing Cu_2O_2 cores depends on various structural features such as the coordination geometry of the copper ions, the Cu–O(R)–Cu angle, Cu–O bond lengths, Cu···Cu distances, out-of-plane shift of the phenyl rings or hydrogen atoms in the bridge, and torsion angles.[1a−c] For equatorial–equatorial bridged copper(II) systems, the Cu–O(H)–Cu angle seems to be the most important of these dimensions. In general, antiferromagnetic character is found for complexes with a Cu–O(H)–Cu angle larger than 97°, while ferromagnetism appears for smaller values. The literature data show that, in most of these complexes, this angle is greater than this value, and consequently the coupling is antiferromagnetic.[1d,f] There are only a few ferromagnetically coupled phenoxido/hydroxido-bridged copper(II) complexes.[1f,3−5] For the diphenoxido-bridged complexes, the presence of large substituents in the ligand that creates a large phenyl out-of-plane angle or a large hinge distortion of the Cu_2O_2 framework has been proposed to be responsible for ferromagnetic coupling.[3] In some dihydroxido-bridged complexes, the presence of axially bridging ligands or a large out-of-plane shift of hydrogen atoms created by a weak interaction between hydrogen atoms to anionic ligands and/or solvent molecules is taken into account in order to explain the ferromagnetic coupling.[4,5] Thus, it is a great challenge to design a ferromagnetic copper(II) complex containing double-phenoxido or -hydroxido bridges.

Catechol oxidase is a type III active site protein containing copper that catalyzes the oxidation of a wide range of *o*-diphenols (catechols) to the corresponding *o*-quinones in a process known as catecholase activity.[6] The ability of dicopper complexes to oxidize phenols and catechols is well-known. Various factors such as metal–metal distances, electrochemical

Received: February 13, 2012
Published: September 10, 2012

dx.doi.org/10.1021/ic300319s | *Inorg. Chem.* 2012, 51, 10111−10121

properties of the complexes, exogenous bridging ligands, the ligand structure, and the pH are known to influence the catecholase activity.[2] In the dinuclear complexes, a Cu−Cu distance of 2.9−3.2 Å has been suggested to provide maximum catecholase activity because of the requirement of a steric match between the substrate and catalyst.[7] The number and nature of the bridging ligands between the copper centers in a complex play an important role in the catecholase activity. It is reported that bridging ligands such as hydroxido,[8] alkoxido or phenoxido,[9] and carboxylato[2c,10] enhance but halogen bridges retard the catecholase activity.[11] Regarding the number of bridges, it has been found that double-phenoxido or -hydroxido bridges sometimes lead to a catalytically inactive species,[8b] but these may be taken as exceptional because many other similar double-bridged compounds show considerable catalytic activity.[8b,9a−c,12] Moreover, there are two possible mechanisms for the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) to 3,5-di-*tert*-butylquinone (3,5-DTBQ). The first one proceeds through the reaction between the dicopper(II) species and substrate to form one molecule of quinone and a dicopper(I) species, which subsequently reacts with an oxygen molecule to generate a peroxodicopper(II) adduct, which then oxidizes a second molecule of the substrate to quinone. Water is produced as a byproduct by this four-electron-reduction process.[13] The second mechanism involves the formation of a copper(II)−copper(I) semiquinonate as an intermediate species.[8a,12,14] Its subsequent reaction with dioxygen results in the reoxidation of the copper(I) ion and release of the quinone molecule and hydrogen peroxide in the two-electron-reduction process.[8d] However, there are disparate views as to whether the formation of hydrogen peroxide is continued during the whole course of the oxidation reaction[8a] or is stopped after a few minutes.[2f] The peroxide can also participate in the catalytic cycle by reoxidizing the reduced dicopper(I) species to dicopper(II) and itself is converted into water.[2f,13]

In this paper, we report the synthesis, crystal structures, magnetic properties, and catecholase activity of two dinuclear copper(II) compounds, $[Cu_2L_2(ClO_4)_2]$ (**1**) and $[Cu_2L_2(OH)]ClO_4$ (**2**), derived from a tridentate reduced Schiff base ligand, 2-[[2-(diethylamino)ethylamino]methyl]-phenol (HL). Compound **1** is a typical antiferromagnetically coupled double-phenoxido-bridged dimer that shows moderate catecholase activity. However, inclusion of an additional hydroxido bridge into this compound results in a novel triple-bridged dinuclear copper(II) complex, **2**, in which the magnetic coupling changes to ferromagnetic. The catecholase activity of **2** is higher than that of **1**, a fact that may be related to the higher pH of its solution. To our knowledge, **2** is the first triple-bridged Cu_2O_3 core whose catecholase activity has been investigated.

■ EXPERIMENTAL SECTION

Materials. The reagents and solvents used were of commercially available reagent quality.

Caution! Perchlorate salts of metal complexes are potentially explosive, and caution should be exercised when dealing with such derivatives.

Synthesis of the Reduced Schiff Base Ligand 2-[[2-(Diethylamino)ethylamino]methyl]phenol (HL). The Schiff base ligand was synthesized by refluxing a solution of salicylaldehyde (0.52 mL, 5 mmol) and *N*,*N*-diethylethylenediamine (0.70 mL, 5 mmol) in methanol (30 mL) for 1 h.[15] The solution was cooled to 0 °C, and solid sodium borohydride (210 mg, 6 mmol) was added slowly to this methanolic solution with stirring. After completion of the addition, the resulting solution was acidified with concentrated HCl (5 mL) and then evaporated to dryness.[16] The reduced Schiff base ligand HL was extracted from the solid mass with methanol, and this methanol solution (ca. 20 mL) was used for the preparation of complexes.

Synthesis of the Complex $[Cu_2L_2(ClO_4)_2]$ (1). An extracted methanolic solution of HL as prepared above was added to a solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.850 g, 5 mmol) in methanol (20 mL). The mixture was stirred for 1 h and filtered. The filtrate was kept undisturbed at room temperature. The resultant solution upon standing overnight at room temperature yielded green single crystals suitable for X-ray analysis. Yield: 1.441 g, 75%. Anal. Calcd for $C_{26}H_{42}Cl_2Cu_2N_4O_{10}$: C, 40.63; H, 5.51; N, 7.29. Found: C, 40.30; H, 5.74; N, 6.95. IR (KBr, cm^{-1}): ν(N−H) 3217, $\nu(ClO_4^-)$ 1047, 1102. λ_{max}, nm (ε_{max}, dm^3 mol^{-1} cm^{-1}; methanol): 650 (407), 424 (2380).

Synthesis of the Complex $[Cu_2L_2(OH)]ClO_4$ (2). Compound **1** (0.768 g, 1 mmol) was dissolved in methanol (10 mL), and triethylamine (0.28 mL, 2 mmol) was added in a 1:2 molar ratio. The mixture was stirred for 1 h and filtered. The filtrate was kept undisturbed at room temperature. The resultant solution upon standing overnight at room temperature yielded green single crystals of **2** suitable for X-ray analysis. Yield: 0.480 g, 70%. Anal. Calcd for $C_{26}H_{43}Cu_2ClN_4O_7$: C, 45.51; H, 6.32; N, 8.16. Found: C, 45.29; H, 6.65; N, 7.92. IR (KBr, cm^{-1}): ν(N−H) 3253, $\nu(ClO_4^-)$ 1090. λ_{max}, nm (ε_{max}, dm^3 mol^{-1} cm^{-1}; methanol): 655 (373), 417 (1838).

Alternative Method for the Synthesis of Complex 2. A methanolic solution of HL (20 mL), prepared using the same quantity of reactant as stated above was added to a solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.850 g, 5 mmol) in methanol (20 mL). Triethylamine (1.05 mL, 10 mmol) was added dropwise to this solution with constant stirring. The mixture was stirred for 1 h and filtered. The filtrate was kept undisturbed at room temperature. The resultant solution upon standing overnight at room temperature yielded green single crystals suitable for X-ray analysis. Yield: 1.235 g, 72%. Anal. Calcd for $C_{26}H_{43}Cu_2ClN_4O_7$: C, 45.51; H, 6.32; N, 8.16. Found: C, 45.17; H, 6.66; N, 7.88. IR (KBr, cm^{-1}): ν(N−H) 3253, $\nu(ClO_4^-)$ 1090. λ_{max}, nm (ε_{max}, dm^3 mol^{-1} cm^{-1}; methanol): 655 (373), 417 (1838).

Catalytic Oxidation of 3,5-DTBC. In order to study the catecholase activity of the complexes, 10^{-4} M solutions of **1** and **2** in methanol were treated with 100 equiv of 3,5-DTBC in methanol under aerobic conditions at room temperature. The absorbance versus wavelength (wavelength scan) of these solutions was recorded at regular time intervals of 5 min in the wavelength range of 300−600 nm. To determine the dependence of the rate on the substrate concentration and various kinetic parameters, a 10^{-4} M solution of complexes was treated with 10, 30, 50, 70, and 100 equiv of substrate. The reactions were followed spectrophotometrically by monitoring the increase in the absorbance at 390 nm (quinone band maximum) as a function of time (time scan).

To detect the formation of hydrogen peroxide during the catalytic reaction, we followed a reported method.[2c] Reaction mixtures were prepared as in the kinetic experiments. During the course of the oxidation reaction, the solution was acidified with H_2SO_4 to pH 2 to stop further oxidation after a certain time and an equal volume of water was added. The formed quinone was extracted three times with dichloromethane. To the aqueous layer were added 1 mL of a 10% solution of KI and three drops of a 3% solution of ammonium molybdate. The formation of I_3^- could be monitored spectrophotometrically because of the development of the characteristic I_3^- band (λ = 353 nm, ε = 26000 M^{-1} cm^{-1}).

Physical Measurements. Elemental analyses (C, H, and N) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra in KBr pellets (4500−500 cm^{-1}) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra in methanol (1200−350 nm) were recorded in a Hitachi U-3501 spectrophotometer. Electrochemical studies were carried out using Sycopel model AEW2 1820F/S instrument. The measurements were performed at 300 K in acetonitrile solutions containing 0.2 M TEAP and a 10^{-3} M complex deoxygenated by bubbling with nitrogen. The working, counter, and reference electrodes used were a platinum wire, a platinum coil, and a saturated calomel electrode, respectively. The electrospray ionization mass spectra (ESI-MS) were recorded on a Micromass Q-TOF mass spectrometer. The magnetic measurements were carried out in the "Unitat de mesures magnètiques dels SCT (Universitat de Barcelona)" on polycrystalline samples (20 mg) with a Quantum Design SQUID MPMSXL magnetometer in applied fields of 10000 and 500 G in the temperature ranges of 2−300 and 2−30 K, respectively. The diamagnetic corrections were evaluated from Pascal's constants.

Crystal Data Collection and Refinement. Crystal data for the two crystals are given in Table 1. A total of 16201 and 11514 independent reflection data were collected with Mo Kα radiation at 150 and 293 K, respectively, using the Oxford Diffraction X-Calibur CCD system. The crystals were positioned at 50 mm from the CCD. A total of 321 frames were measured with a counting time of 10 s. Data analyses were carried out with the *CrysAlis* program.[17] The structures were solved using direct methods with the *SHELXS97* program.[18] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times (or 1.5 times for methyls) those of the atom to which they were attached. Absorption corrections were carried out using the *ABSPACK* program.[19] In **2**, one perchlorate was refined with two sets of positions for the four oxygen atoms, and the other was disordered over two distinct sites; each was refined with 50% occupancy. The structures were refined on F^2 to R1 = 0.0683 and 0.0682 and wR2 = 0.1120 and 0.2228 for 9527 and 7193 data, respectively, with $I > 2\sigma(I)$.

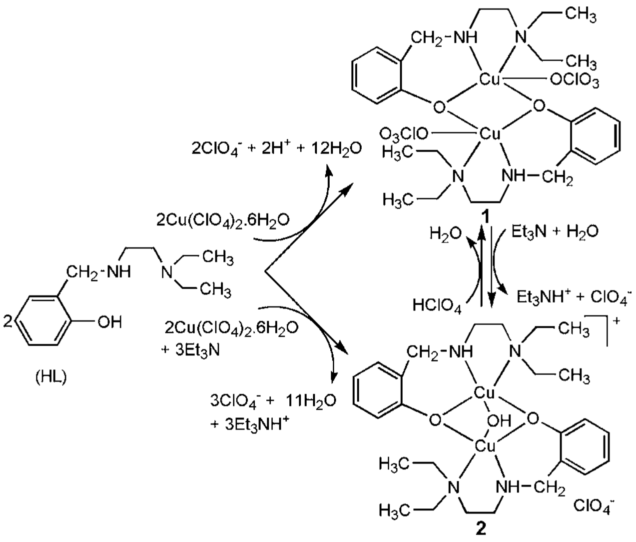
Table 1. Crystal Data and Structure Refinement of Complexes 1 and 2

	1	2
formula	$C_{26}H_{42}Cl_2Cu_2N_4O_{10}$	$C_{26}H_{43}Cu_2ClN_4O_7$
M	768.64	686.17
cryst syst	orthorhombic	triclinic
space group	$P2_1ca$	$P\bar{1}$
a/Å	39.388(2)	12.912(4)
b/Å	8.7010(5)	13.044(4)
c/Å	18.2535(8)	19.528(6)
α/deg	90	81.778(4)
β/deg	90	84.012(4)
γ/deg	90	89.282(4)
V/Å^3	6255.8(6)	3237.4(17)
Z	8	4
D_c/g cm^{-3}	1.632	1.408
μ/mm^{-1}	1.591	1.442
F(000)	3184	1432
R(int)	0.110	0.048
total reflns	33822	23371
unique reflns	16201	11514
$I > 2\sigma(I)$	9527	7193
R1, wR2	0.0683, 0.1120	0.0682, 0.2228
temp/K	150	293

■ RESULTS AND DISCUSSION

Synthesis of the Complexes. The condensation of *N,N*-diethylethylenediamine in a 1:1 molar ratio with salicylaldehyde afforded the Schiff base 2-[[2-(diethylamino)ethylimino]-methyl]phenol, which upon reduction with sodium borohydride readily produced the reduced Schiff base HL (Scheme 1). HL upon reaction with copper(II) perchlorate in a 1:1 molar ratio yielded the diphenoxido-bridged compound **1**. It is to be noted that the formation of such diphenoxido-bridged copper(II) dimers is a very common feature for the complexes of copper(II) with NNO-donor Schiff bases or reduced Schiff bases.[1h−j,20] However, a unique feature of the present work is that when a methanolic solution of compound **1** is treated with triethylamine in a 1:2 molar ratio, a hydroxido group coordinates to the equatorial positions of both copper(II) atoms and consequently acts as an additional bridge to result in a very rare three-single-atom (two phenoxido and one hydroxido)-bridged copper(II) dimer. Compound **2** can be produced directly by reacting HL and copper(II) perchlorate in the presence of triethylamine (2:2:3 molar ratio) in a methanol solution. Complex **1** was also obtained by adding $HClO_4$ to a methanolic solution of complex **2** in a 1:1 molar ratio. In this context, it should be noted that unreduced N,N,O-donor Schiff bases upon reaction with copper(II) perchlorate in the presence of triethylamine, i.e., by a method that is similar to the synthesis of **2**, produces μ_3-OH-bridged trinuclear copper(II) complexes.[21]

Scheme 1. Formation of the Complexes



IR and Electronic Spectra. A moderately strong, sharp peak due to a N−H stretching vibration, at 3217 and 3253 cm^{-1} for complexes **1** and **2**, respectively, shows that the imine group of the Schiff base is reduced. This reduction is also very clearly indicated by the absence of the strong band due to imine vibration, which appears in the region 1620−1650 cm^{-1} for the complexes of the unreduced Schiff bases.[22] In complex **2**, there is a single band at 3575 cm^{-1}, indicating the presence of a hydroxido group. The IR spectra show bands due to the ν_3 mode of perchlorate stretching at 1047 and 1102 cm^{-1} for complex **1** and a single band at 1090 cm^{-1} for complex **2**, corroborating the presence of coordinated and ionic perchlorate, respectively.

The electronic spectra of these two compounds were recorded in a methanolic solution as well as in the solid state (Figure S1 in the Supporting Information). In methanol solutions, the electronic spectra show single absorption bands at 650 and 655 nm due to a d−d transition for compounds **1** and **2**, respectively. In the higher-energy region, the ligand-to-metal charge-transfer band was located for compound **1** at 424 nm, which is at a higher wavelength than that of compound **2** at 417 nm. Upon the addition of an increasing amount of triethylamine to the solutions of the complexes, these bands gradually shifted to lower wavelength regions for both complexes (Figures S2 and S3 in the Supporting Information). In the solid state, the electronic spectra show d−d transition bands at 600 and 650 nm and ligand-to-metal charge-transfer bands at 426 and 417 nm for compounds **1** and **2**, respectively. The electronic spectral data for both of the complexes were found to be almost identical in solutions, although the solid-state spectra show some differences. Therefore, the different structural identities of **1** and **2** that have been found in the solid state are probably lost in the solution.

Crystal Structures of Complexes 1 and 2. The structure of **1** contains two molecules in the asymmetric unit, called A and B, with equivalent structures of the formula $[Cu_2L_2(ClO_4)_2]$. The structure of A is shown in Figure 1, together with the atomic numbering scheme. Dimensions in the metal coordination spheres of A and B are given in Table 2.

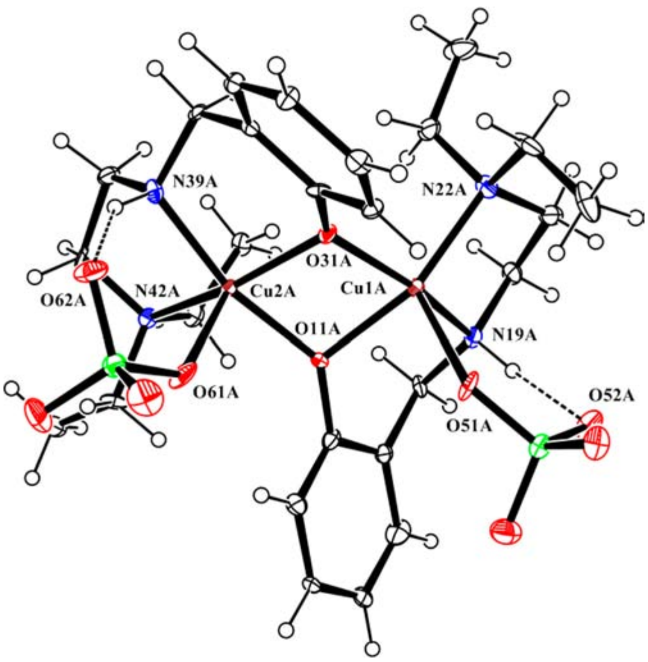


Figure 1. Structure of molecule A in **1** with ellipsoids at 30% probability. Hydrogen bonds are shown as dotted lines. The structure of molecule B is equivalent.

In each dimer, the two metal atoms are bonded to three donor atoms of one ligand L and the oxygen atom of a second ligand L, which therefore bridges both metals. These four atoms form an equatorial plane, and in addition, there is a perchlorate oxygen atom in an axial position, thus completing a square-pyramidal structure. The Addison parameter (τ)[23] of the pentacoordinated copper(II) is 0.09 (average), indicating that the geometry around the metal is slightly distorted square pyramidal. Bond lengths from the metal to donor atoms of the ligand are in the ranges 1.991(6)−2.007(6) Å to secondary nitrogen and 2.031(6)−2.053(5) Å to tertiary nitrogen. There is little difference between the bond lengths to the two bridging oxygen atoms with all Cu−O distances in the range 1.945(5)−1.978(5) Å. The axial bond lengths to the perchlorate oxygen atom are in the range 2.316(5)−2.356(6) Å. The four donor atoms in the equatorial plane show root-mean-square (rms) deviations of 0.064, 0.092, 0.051, and 0.071 Å, with the copper atoms 0.343(3), 0.279(3), 0.334(3), and 0.288(3) Å from the relevant planes for Cu1A, Cu2A, Cu1B, and Cu2B, respectively, in the direction of the axial atom. In the dimers, the two equatorial planes intersect at 46.2(1)° for A and 45.6(1)° for B, thus allowing the two copper atoms to be in close proximity at 3.016(1) Å in A and 3.020(1) Å in B.

Table 2. Bond Distances (Å) and Angles (deg) in the Metal Coordination Spheres for Complex 1

	A	B
Cu1−O31	1.956(5)	1.978(5)
Cu1−O11	1.968(5)	1.946(5)
Cu1−N22	2.031(6)	2.036(6)
Cu1−N19	2.007(6)	2.003(6)
Cu1−O51	2.345(5)	2.350(5)
Cu1−Cu2	3.016(1)	3.020(1)
Cu2−O11	1.945(5)	1.939(5)
Cu2−O31	1.972(5)	1.974(4)
Cu2−N39	1.991(6)	2.001(6)
Cu2−N42	2.053(5)	2.040(5)
Cu2−O61	2.356(6)	2.316(5)
O31−Cu1−O11	76.7(2)	76.5(2)
O31−Cu1−N19	161.9(2)	161.4(2)
O31−Cu1−N22	97.8(2)	98.5(2)
O31−Cu1−O51	99.0(2)	99.0(2)
O11−Cu1−N19	92.1(2)	91.7(2)
O11−Cu1−N22	156.5(3)	157.5(2)
O11−Cu1−O51	88.7(2)	88.3(2)
N19−Cu1−N22	86.9(2)	86.9(2)
N19−Cu1−O51	94.8(2)	94.8(2)
N22−Cu1−O51	114.9(2)	114.2(2)
O11−Cu2−O31	76.9(2)	76.7(2)
O11−Cu2−N39	165.9(2)	164.3(2)
O11−Cu2−N42	99.8(2)	99.4(2)
O11−Cu2−O61	95.0(2)	94.7(2)
O31−Cu2−N39	92.3(2)	91.7(2)
O31−Cu2−N42	158.7(2)	159.3(2)
O31−Cu2−O61	98.4(2)	94.1(2)
N39−Cu2−N42	87.0(2)	87.6(2)
N39−Cu2−O61	95.6(2)	96.8(2)
N42−Cu2−O61	102.9(2)	106.6(2)
Cu1−O11−Cu2	100.9(2)	102.1(2)
Cu1−O31−Cu2	100.4(2)	99.7(2)

The bonding of the perchlorate is facilitated by the formation of a hydrogen bond between an oxygen atom and the secondary nitrogen in the ligand. Thus, dimensions of N···O, N−H···O, and H···O for N19−H19 to O52 are 2.982(8) Å, 153°, 2.14 Å in A and 2.973(8) Å, 153°, and 2.13 Å in B, and those of N39−H39···O62 are 2.924(9) Å, 147°, and 2.12 Å in A and 2.957(9) Å, 152°, and 2.12 Å in B.

The structure of **2** contains two $[Cu_2L_2(OH)]^+$ cations together with two perchlorates, one of which is disordered over two distinct sites. The two cations, called A and B, have equivalent geometries, described in Table 3, and the structure of cation A is shown in Figure 2.

Each dimer contains two equivalent copper atoms both with pentcoordinate square-pyramidal environments. The metals are bonded to three donor atoms of ligand L together with a hydroxido, which bridges the two metal atoms that constitute the equatorial planes. Like **1**, the tridentate ligand L coordinates to the metal ion in a meridional configuration. The equatorial planes show a slight tetrahedral distortion with rms deviations of 0.104, 0.120, 0.108, and 0.130 Å, respectively, for Cu1A, Cu2A, Cu1B, and Cu2B. The metal atoms are 0.030(5), 0.041(5), 0.043(5), and 0.038(5) Å from the respective equatorial planes. In the dimers, the two square planes intersect at 56.8(3)° for A and 55.8(3)° for B, thus allowing the two

Table 3. Bond Distances (Å) and Angles (deg) in the Metal Coordination Spheres for Complex 2

	A	B
Cu1−O1	1.931(7)	1.937(7)
Cu1−O11	1.949(8)	1.925(8)
Cu1−N19	1.977(9)	1.993(10)
Cu1−N22	2.083(9)	2.071(9)
Cu1−O31	2.448(7)	2.447(8)
O1−Cu1−O11	84.4(3)	85.3(3)
O1−Cu1−N19	174.9(4)	175.6(4)
O1−Cu1−N22	97.3(4)	96.3(4)
O11−Cu1−N19	93.3(4)	92.7(4)
O11−Cu1−N22	172.3(4)	171.2(4)
N19−Cu1−N22	85.6(4)	86.2(4)
Cu2−O1	1.937(7)	1.934(7)
Cu2−O31	1.945(8)	1.944(7)
Cu2−N39	1.981(10)	1.990(9)
Cu2−N42	2.062(10)	2.066(10)
Cu2−O11	2.445(8)	2.453(8)
Cu2−Cu1	2.804(2)	2.792(2)
O1−Cu2−O31	85.2(3)	85.8(3)
O1−Cu2−N39	175.1(4)	174.4(4)
O1−Cu2−N42	96.6(4)	96.0(4)
O31−Cu2−N39	93.4(4)	92.9(4)
O31−Cu2−N42	170.6(4)	170.2(4)
N39−Cu2−N42	85.5(4)	86.2(4)
Cu1−O11−Cu2	78.4(3)	78.3(3)
Cu1−O31−Cu2	78.4(3)	78.1(3)
Cu1−O1−Cu2	93.8(3)	92.4(3)

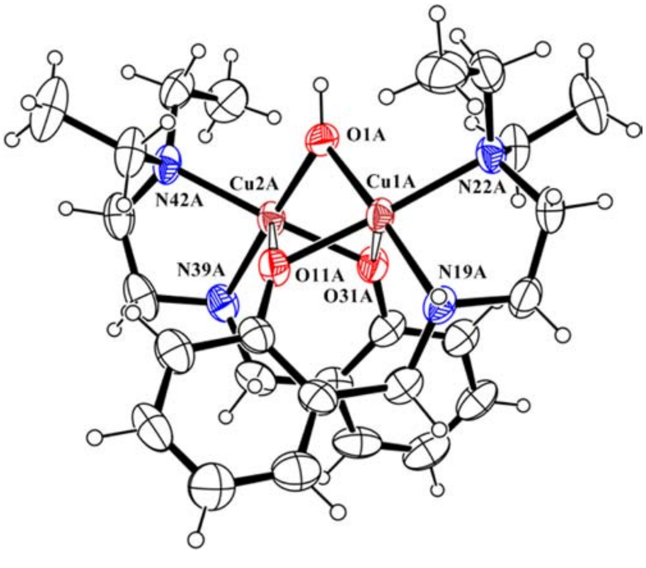


Figure 2. Structure of cation A in **2** with ellipsoids at 30% probability. The structure of cation B is equivalent. The weak axial bonds are shown as open bonds.

copper atoms to be in closer proximity at 2.804(2) Å in A and 2.792(2) Å in B than is found in **1**. Dimensions around all four copper atoms in the two cations are equivalent with bond lengths to bridging hydroxido O1 in the range 1.915(8)−1.934(7) Å, ligand oxygen 1.937(7)−1.948(8) Å, secondary nitrogen 1.977(9)−1.993(10) Å, and tertiary nitrogen 2.062(10)−2.083(9) Å. In addition, there is a weak interaction in an approximate axial position to the oxygen atom of the second ligand, thus giving Cu1−O31 of 2.448(7) and 2.447(8) Å and Cu2−O11 of 2.445(8) and 2.453(8) Å in A and B, respectively. The Addison parameter (τ) of the pentacoordinated copper(II) is 0.06 (average), indicating that the geometry around the metal is slightly distorted square pyramidal. The bond lengths in the equatorial plane are slightly smaller than those in complex **1**, but axial bond lengths are greater.

The secondary nitrogen forms hydrogen bonds to oxygen atoms of the disordered perchlorate centered on Cl6, from cation A to oxygen atoms in one orientation and from cation B to oxygen atoms in the other (Figure 3). Dimensions for N···O, N−H···O, and H···O are as follows: for N19A−H19A to O66^a (a = x, y − 1, z), 3.17(3) Å, 160°, and 2.27; for N39A−H39A to O68, 3.08(3) Å, 166°, and 2.19 Å; for N19B−H19B to O62^b (b = x + 1, y, z), 3.11(3) Å, 172°, and 2.21 Å; for N39B−H39B to O64, 3.19(3) Å, 166°, and 2.30 Å. The two hydroxides also form hydrogen bonds but to the perchlorate disordered over two sites: O1A−H1A to O82^c (c = 1 − x, −y, −z), 2.86(3) Å, 158°, and 1.97 Å; O1B−H1B to O73, 2.93(3) Å, 146°, and 2.11 Å (Table 4).

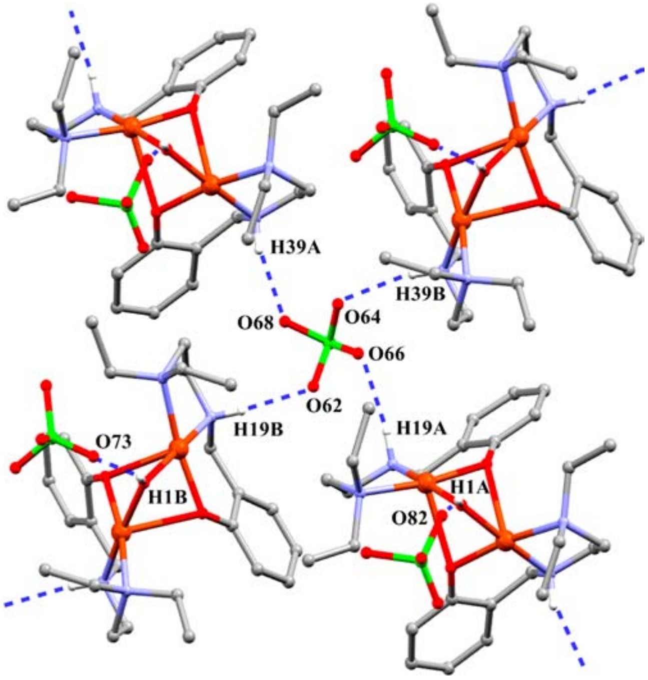


Figure 3. Hydrogen bonding in the polymeric structure of compound **2** (all hydrogen atoms except H1, H19, and H39 are omitted for clarity).

Magnetic Properties. Temperature-dependent molar susceptibility measurements of powdered samples **1** and **2** were carried out in an applied field of 10000 G for **1** and 7000 G for **2** and also 500 G for **1** and 400 G for **2** in the temperature ranges of 2−300 and 2−30 K, respectively. The χ_mT vs T plots of complexes **1** and **2** are shown in Figures 4 and 5, respectively; in both cases, χ_mT is the magnetic susceptibility per Cu_2 unit. At room temperature, the χ_mT values of **1** and **2** are 0.15 and 0.85 $cm^3\ mol^{-1}$ K, values that are respectively considerably less and slightly higher than the 0.75 $cm^3\ mol^{-1}$ K calculated for two uncoupled $S = {}^1/_2$ spins (g = 2.00). When the samples are cooled, the χ_mT values decrease

Table 4. Hydrogen-Bonding Distances (Å) and Angles (deg) for Complexes 1 and 2[a]

complex	D−H···A	D−H (Å)	A···H (Å)	D···A (Å)	∠D−H−A (deg)
1	N19A−H19A···O52A	0.91	2.14	2.982(8)	153
	N19B−H19B···O52B	0.91	2.13	2.973(8)	153
	N39A−H39A···O62A	0.91	2.12	2.924(9)	147
	N39B−H39B···O62B	0.91	2.12	2.957(9)	152
2	N19A−H19A···O66[a]	0.91	2.27	3.17(3)	169
	N19B−H19B···O62[b]	0.91	2.21	3.11(3)	172
	N39A−H39A···O64	0.91	2.3	3.19(3)	166
	N39B−H39B···O68	0.91	2.54	3.26(3)	136
	O1A−H1A···O82[c]	0.93	1.97	2.86(3)	158
	O1B−H1B···O73	0.93	2.11	2.93(3)	146

[a] D = donor atom; A = acceptor atom. Symmetry operations: a, *x*, *y* − 1, *z*; b, *x* + 1, *y*, *z*; c, 1 − *x*, −*y*, −*z*.

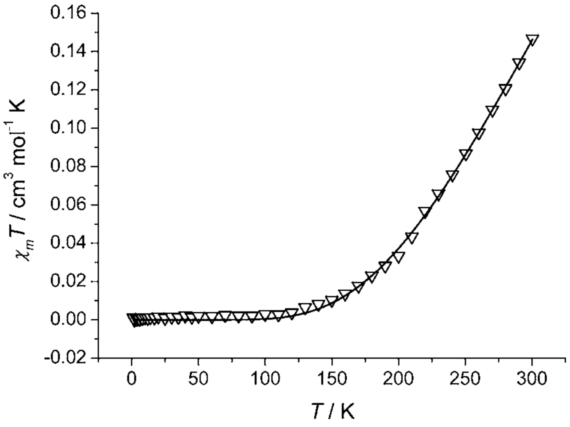


Figure 4. Plot of $\chi_m T$ vs T in the range 2−300 K for **1**.

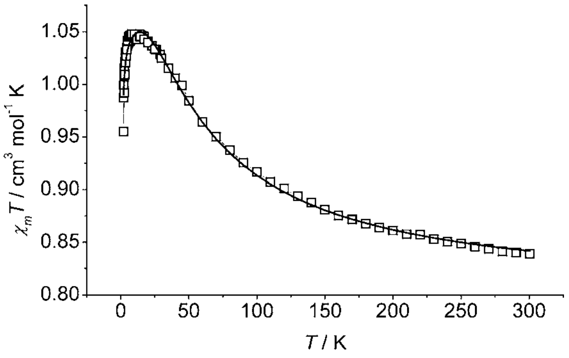


Figure 5. Plot of $\chi_m T$ vs T in the range 2−300 K for **2**.

nearly to zero at 120 K in compound **1**, indicating strong antiferromagnetic coupling between copper(II) ions. However, in the case of compound **2**, when the temperature is lowered, the $\chi_m T$ values increase gradually to reach a maximum value of 1.048 cm^3 mol^{-1} K at 8 K, a behavior that is typical for a ferromagnetically coupled dinuclear copper(II) compound. Below this temperature, the $\chi_m T$ values decrease to a value of 0.955 cm^3 mol^{-1} K at 2 K, a drop that may originate from intermolecular antiferromagnetic interactions.

The strong antiferromagnetic coupling in **1** leads to a diamagnetic ($S = 0$) ground state, as confirmed by the isothermal magnetization measurements at 2 K, which show a value of 0.013 Nμ_B at 5 T (Figure S4 in the Supporting Information). On the contrary, the isothermal magnetization measurements at 2 K for compound **2** confirm the presence of ferromagnetic coupling with a $S = 1$ ground spin state (Figure S4 in the Supporting Information). Its magnetization value tends to 2.0 Nμ_B at 5 T, and it is not yet saturated.

Assuming the isotropic Hamiltonian $H = -JS_1S_2$, the experimental data were fitted to the equation given in the literature for dinuclear copper compounds.[24]

$$\chi = 2Ng^2\beta^2\left[kT - \frac{2zJ'}{3 + \exp(-J/kT)}\right]^{-1}$$

$$[3 + \exp(-J/kT)]^{-1}$$

The parameters *N*, *g*, *β*, *k*, and *T* in the equation have their usual meanings, while *J* = singlet−triplet splitting and *zJ′* is the interaction between neighboring dinuclear identities. The best-fit parameters for reproducing satisfactorily the experimental data, as shown in Figures 4 and 5, are $J = -615.6(6.1)$ cm^{-1} and $g = 2.07$ with $R = 8.69 \times 10^{-4}$ for **1** (the parameter *zJ′* was considered to be equal to zero) and $J = 50.1(1.4)$ cm^{-1}, $g = 2.06$, and $zJ' = -0.15$ cm^{-1} with $R = 3.30 \times 10^{-5}$ for **2** ($R = \sum_i(\chi T_{i,\text{calc}} - \chi T_{i,\text{exp}})^2/\sum_i(\chi T_{i,\text{exp}})^2$).

Magnetostructural Correlations. The magnetic properties of dinuclear copper complexes containing a Cu_2O_2 core depend on its structural properties. Several parameters, such as the coordination geometry of the copper ions, the Cu−O−Cu angle, the Cu−O bond lengths, the Cu···Cu distances, and the torsion angle, have been postulated in the literature as influencing the *J* values of the spin coupling in diphenoxido-bridged dinuclear copper(II) complexes.[1a,b] It has been shown that the overlap between the metal and phenoxido bridging oxygen is a factor that controls spin coupling and is correlated not only with the bridging angle but also with the M−O bond distances. A literature survey of phenoxido-bridged dinuclear copper(II) complexes reveals that when the Cu−O bond distance is less than 1.98 Å, strong antiferromagnetic coupling is observed and the strength of this coupling is linearly dependent on the Cu−O bond distances.[1b] The conformation of the phenyl rings is also important: in the syn conformation, the out-of-plane shift of the phenyl ring can influence the magnetic coupling significantly.[1a] Another important structural factor in pentacoordinated copper(II) complexes is the Addison parameter (*τ*) because an increase in *τ* can be correlated with a decrease in the antiferromagnetic coupling.[22] The strong antiferromagnetic coupling in **1** is anticipated considering the low value of $\tau = 0.09$ (average), the large Cu−O−Cu angle of 100.75° (average), the short Cu−O distance of 1.960 Å (average), and finally the syn conformation of the phenyl groups with an out-of-plane shift of the phenyl ring of 26.05° (average).

In the literature, numerous diphenoxido-bridged copper(II) complexes have been reported, but only 11 contained an additional bridge between the two copper(II) atoms to make the complexes triple-bridged.[20,25] In nine of them, the additional bridge is formed through three atoms of polyatomic coordinated ligands like acetate, perchlorate, nitrate, etc.,[25] but only in two complexes are there single-atom bridges via the oxygen atom of a methanol or water molecule.[20] However, in all such triple-bridged complexes, the phenoxido-bridged Cu_2O_2 core remained equatorial−equatorial and the additionally coordinated ligand occupied the axial position. As a consequence, in all such cases, the magnetic orbitals $d_{x^2-y^2}$ of

Table 5. Magnetostructural Data for Antiferromagnetic Dicopper(II) Complexes with a Single Hydroxido Bridge[a]

compound	Cu···Cu (Å)	Cu−O−Cu (deg)	J (cm^{-1})	geometry	reference
$[Cu_2(bpy)_4(OH)](ClO_4)_3$	3.645	141.60	−322	Tbpeq	27b
$Na[Cu_2(L^1)_2(OH)]\cdot 2H_2O$	3.437	131.11	−334	Spl	27a
$K[Cu_2(L^1)_2(OH)]\cdot 0.2H_2O$	3.370	125.74	−296	Spl	27a
$[Cu_2(L^2)(OH)](ClO_4)_3\cdot 1.5H_2O$	3.740	150.60	−510	Tbpax	27c
$[Cu_2([22]py4pz)OH](ClO_4)_3\cdot H_2O$	3.757	155.97	−691	Tbpax	1g
$[Cu_2(L^3)(OH)(ClO_4)](ClO_4)_2\cdot CHCl_3$	3.642	143.7	−500	Spy	27d
$[Cu_2(L^4)(OH)](CF_3SO_3)_3$	3.90	174.0	−865	Tbpax	27e
$[Cu_2(L^5)(dpm)(OH)](ClO_4)_3\cdot 2H_2O$	3.663	137.9	−360	Spy	27g
$[Cu_2(L^6)(OH)](ClO_4)_2\cdot H_2O$	3.57	141.7	−240	Spy	27h
$[Cu_2(dien)_2(ClO_4)_3(OH)]$	3.435	128.1	−374	Spl	27i
$[Cu_2(terpy)_2(H_2O)(ClO_4)_3(OH)]$	3.642	145.7	−303	Spy	27j
$[Cu_2(L^7)(OH)](CF_3SO_3)(BPh_4)_2$	3.89	166.1	−880	Tbpeq	27k
$[Cu_2L_2(OH)]ClO_4$	2.798	93.10	50	Spy	this work

[a] Spl = square planar, Spy = square pyramidal with OH^- in the equatorial position, Tbpax = trigonal bipyramidal with OH^- in the axial position, and Tbpeq = distorted trigonal bipyramidal with OH^- in the equatorial position. Abbrevations: H_2L^1 = 2,6-bis[*N*-(phenyl)carbamoyl]pyridine; L^2 = tetraimine Schiff base of tris(2-aminoethyl)amine and 2,5-diformylfuran; L^3 = 1,4,7,13,16,19-hexaaza-10,22-dioxatetracosane; L^4 = octaamine from BH_4^- reduction of the Schiff base of tris(2-aminoethyl)amine and 2,5-diformylfuran; L^5 = 1,1,2,2-tetrakis(2-pyridyl)ethylene; dpm = bis(2-pyridyl)methane; L^6 = Schiff base of 2,6-diacetylpyridine and 3,6-dioxooctane-1,8-diamine; L^7 = partially hydrolyzed Schiff base of 2,6-diacetylpyridine and tris(2-aminoethyl)amine; HL = 2-[[2-(diethylamino)ethylamino]methyl]phenol; dien = diethylenetriamine; terpy = 2,2′;6′,2″-terpyridine; tpmc = 1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane.

the two copper(II) atoms interact via the diphenoxido bridge, whereas the axially coordinated bridged atom does not contribute significantly toward magnetic coupling. Therefore, magnetic interactions through $Cu-O_w$ or $Cu-O_{MeOH}$ of the two dinuclear triply oxido-bridged copper(II) complexes[20] can be considered to be negligible because the distances are too long and the corresponding oxygen atoms are coordinated at the axial positions. The magnetic interaction in both compounds is antiferromagnetic, as is expected for bis(μ-phenoxido)dicopper complexes. In addition, another dinuclear copper(II) complex,[1d] containing two short hydroxido bridges and an additional H_2O bridge with a long axial distance, is reported. The magnetic interaction in this compound is very weak and antiferromagnetic.

Our present complex **2** is unique in that the additional hydroxido group forms an equatorial−equatorial bridge between the two square-pyramidal copper(II) atoms, whereas the diphenoxido bridges are axial−equatorial with the long axial bonds at 2.446 Å (average). In square-pyramidal copper(II), the equatorial bond lengths are shorter than the axial bond lengths, indicating that the spin-unpaired electron is located in the $d_{x^2-y^2}$ orbital and that the d_{z^2} orbital contains spin-paired electrons. Therefore, to a first approximation, in compound **2**, the coupling between two copper(II) atoms through the equatorial−axial phenoxido bridges can be neglected. Consequently, from a magnetic point of view, the compound can be considered as a single hydoxido-bridged dimer with a Cu−O(H)−Cu angle of 93.10° (average) and Cu−O(H) distances of 1.928 Å (average).

A limited number of dihydroxido-bridged copper(II) complexes have been reported[1d,f,4,5] but most of them exhibited relatively strong antiferromagnetic coupling.[1d,f] Magnetostructural correlations in dinuclear copper(II) complexes, bridged equatorially by pairs of hydroxido groups, show that the major factor controlling spin coupling between the $S = {}^1/_2$ metal centers is the Cu−O(H)−Cu angle. In particular, Hatfield and Hodgson[5d] have shown that the experimentally determined singlet−triplet energy gap (J) varies linearly with the Cu−O(H)−Cu angle, and subsequently a theoretical justification of this result was proposed by Hoffmann and co-workers.[26] In such complexes, a transition from antiferromagnetism to ferromagnetism is observed for Cu−O(H)−Cu angles smaller than 97° because of an "accidental orthogonality" of the orbitals bearing the unpaired electrons.[5d] According to Ruiz et al., there are two possible mechanisms accountable for the exchange interaction in the hydroxo-bridged dinuclear copper(II) complexes: direct interaction between the copper atoms and superexchange interaction through the hydroxido bridge.[1c] In compound **2**, two additional axial−equatorial phenoxido bridges, although not very effective in magnetic coupling, seem to cause a decrease in the Cu···Cu distance, which, in turn, reduces the Cu−O(H)−Cu angle below 97°, and the coupling becomes ferromagnetic. The literature data show that, although there are few ferromagnetically coupled double hydroxido-bridged copper(II) dimers (Table S1 in the Supporting Information),[4,5] in all of the single hydroxido-bridged dicopper(II) complexes that have been reported so far, the Cu−O(H)−Cu angles are above the limit, causing moderate to strong antiferromagnetic coupling (Table 5) between the metal ions.[1g,27] Thus, to the best of our knowledge, compound **2** is the first example of a copper(II) dimer in which ferromagnetic coupling takes place through the single hydroxido bridge. In summary, we can conclude that the magnetic results obtained for complex **1** are in accordance with the literature data, and the ferromagnetic behavior of complex **2** is probably due to the small Cu−O−Cu angle of 93.10°.

Kinetic Studies for Catecholase Activity. In most studies of the catecholase activity of model complexes, 3,5-DTBC has been chosen as the substrate. The oxidation product 3,5-di-*tert*-butylquinone (3,5-DTBQ) is very much stable and exhibits a maximum absorption at 390 nm in pure methanol. Prior to a detailed kinetic study, it is necessary to check the ability of the dinuclear complexes to oxidize 3,5-DTBC. For this purpose, 10^{-4} M solutions of complexes **1** and **2** were treated with 100 equiv of 3,5-DTBC under aerobic conditions in a methanol solution. Immediately after the addition of substrate 3,5-DTBC to the solutions of the catalysts, the absorption peak at 390 nm (ε = 1900 M^{-1} cm^{-1}), which is indicative of oxidation from 3,5-

DTBC corresponding to quinone (3,5-DTBQ), increased in size, thus showing considerable catecholase activity, as shown in Figures 6 (for complex **2**) and S5 in the Supporting Information (for complex **1**), when compared to the inactive $Cu(ClO_4)_2 \cdot 6H_2O$ (Figure S6 in the Supporting Information). Plots of absorbance versus wavelength for complexes **1** and **2** with the same time interval are shown in Figure S7 in the Supporting Information.

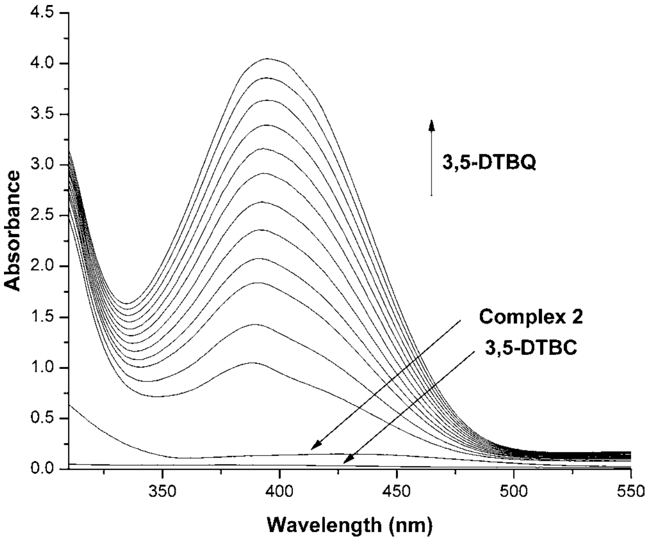


Figure 6. Increase in the absorbance after the addition of 100 equiv of 3,5-DTBC to a methanolic solution containing complex **2** (10^{-4} M). The spectra were recorded every 5 min.

The kinetic study of the oxidation of 3,5-DTBC to 3,5-DTBQ by the complexes was carried out by monitoring the increase in the absorbance at 390 nm by the initial rate method. The rate constant for a particular complex−substrate mixture was determined from the $\log[A_\alpha/(A_\alpha - A_t)]$ versus time plot. To determine the dependence of the rates on the substrate concentration and various kinetic parameters, solutions of complexes **1** and **2** were studied using increasing concentrations of 3,5-DTBC (from 10 to 100 equiv) under aerobic conditions at a complex concentration of 10^{-4} M. A first-order dependence was observed at low concentrations of the substrate, whereas saturation kinetics were found at higher concentrations of the substrate for all of the complexes shown in Figures 7 (for complex **2**) and S8 in the Supporting Information (for complex **1**). This dependence on the substrate concentration indicates a catalyst−substrate binding to be an initial step in the catalytic mechanism. A treatment on the basis of the Michaelis−Menten approach, originally developed for enzyme kinetics, was therefore applied and linearized by means of a Lineweaver−Burk plot to calculate various kinetic parameters such as the Michaelis−Menten constant (K_M) and the maximum initial rate (V_{max}).[28] The k_{cat} values can be calculated by dividing the V_{max} values by the concentration of the corresponding complexes.

The data obtained from the Lineweaver−Burk plot model are used for a comparison of the catalytic activity toward the oxidation of 3,5-DTBC, as shown in Table 6. It is to be noted that the catecholase activity of compound **2** is higher than that of compound **1**. The results are, at first sight, inconsistent with earlier findings. In the dinuclear complexes, the Cu−Cu distances of 2.9−3.2 Å are supposed to give maximum catecholase activity owing to the requirement of a steric match between the substrate and catalyst.[2a] Wei et al. reported that, within a series of oxygen-atom-bridged dicopper(II) complexes, the highest catalytic activity was observed with metal−metal distances of 2.9−3.0 Å, which were close to that observed (2.9 Å) for the metal form of catechol oxidase, and the compound that contained a Cu···Cu distance of 2.80 Å gave the lowest catecholase activity.[9b] When the present two complexes are compared, the higher catecholase activity of complex **2**, which has a very short Cu···Cu distance (average 2.798 Å) compared to that (average 3.018 Å) of **1**, is at first sight surprising. However, if we consider the presence of the OH bridge, which has been found to enhance the catecholase activity of some compounds,[2g,29] the results can be explained. In fact, the UV−vis spectra suggest that in solution both compounds produce identical species. However, the pH measurements reveal a higher value for the solution of **2**, which is expected because of the presence of a OH group. Again, regardless of whether **1** or **2** is used as the precatalyst, the catecholase activity increases with increasing pH of the solutions until pH 8.20 (Figure S9 in the Supporting Information) and thereafter self-oxidation of 3,5-DTBQ becomes very fast. This pH dependence may be due to the fact that in alkaline media the catechol undergoes deprotonation, and consequently its coordination to the metal centers is facilitated. Therefore, the higher catecholase activity of **2** may be assumed to be simply due to the higher pH of its solution.

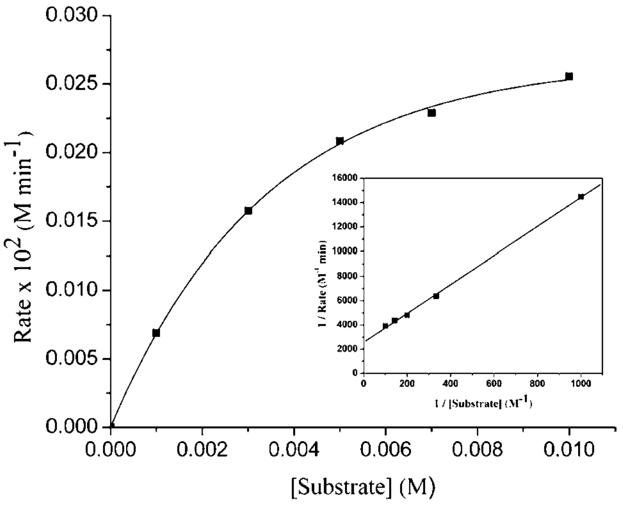


Figure 7. Plot of the initial rates versus substrate concentrations for the oxidation reaction catalyzed by complex **2**. The inset shows the Lineweaver−Burk plot.

To establish the pathway for the catalytic reaction, we checked whether dioxygen was reduced to water (as in the enzyme) or to H_2O_2, as is found in various model systems. The presence of hydrogen peroxide was clearly detected by the oxidation of I^- (see the Experimental Section) using a 1×10^{-2} M concentration of catechol with a catalyst concentration of 1×10^{-4} M for both compounds (Figure S10 in the Supporting Information). During the course of the catalytic reaction, the amount of H_2O_2 was also estimated. It was found that for both compounds dihydrogen peroxide is formed at the initial stage of the reactions and its concentration remains almost constant, although the oxidation of 3,5-DTBC continues (Figure 8). After 1 h, the amount of H_2O_2 is only about 30% and 20% of 3,5-DTBQ formed for compounds **1** and **2**, respectively. A

Table 6. Kinetic Parameters for Complexes **1** and **2**

complex	V_{max} (M min^{-1})	K_M (M)	k_{cat} (h^{-1})	K_{ass} (M^{-1})	K_{cat}/K_M (M^{-1} h^{-1})
1	$(1.56 \pm 0.03) \times 10^{-4}$	$(3.32 \pm 0.06) \times 10^{-3}$	93.6	301.2	28.2×10^3
2	$(3.89 \pm 0.17) \times 10^{-4}$	$(4.60 \pm 0.20) \times 10^{-3}$	233.4	217.4	50.7×10^3

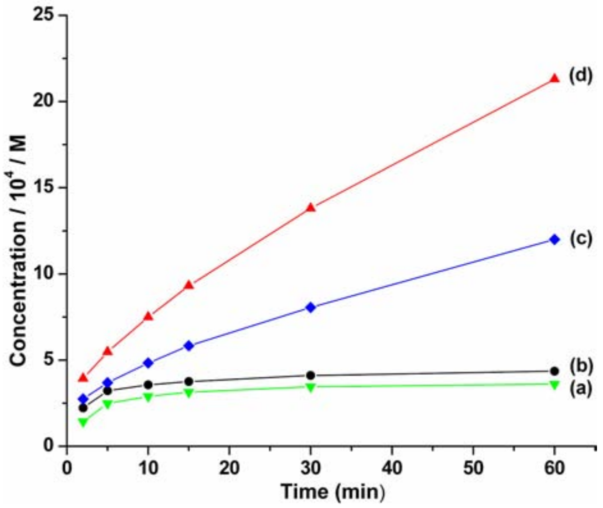


Figure 8. Course of 3,5-DTBQ and H_2O_2 formation during the catalytic reaction at substrate-to-catalyst ratios of 100:1: (a and b) H_2O_2 concentrations and (c and d) 3,5-DTBQ concentrations for compounds **1** and **2**, respectively.

similar result was obtained by Reedijk et al.,[2f] and they proposed two different mechanisms: initially reduction of dioxygen to dihydrogen peroxide and then to water are probably operative during the catalytic oxidation.

To obtain a mechanistic inference of the catecholase activity and to investigate possible complex−substrate intermediates, we recorded ESI-MS spectra of both complexes and a 1:100 mixture of the complexes and 3,5-DTBC within 10 min of mixing in a methanol solvent (Figures S11−S20 in the Supporting Information). The spectra of complexes **1** and **2** show a base peak at *m*/*z* 283.9 (100%), which can be assigned to the mononuclear species $[CuL]^+$. Other peaks at *m*/*z* 604.9 and 668.8 indicate the presence of the dinuclear species $[Cu_2L_2Cl]^+$ and $[Cu_2L_2(ClO_4)]^+$, respectively. There is also another peak at *m*/*z* = 642.9 in complex **2** indicating the presence of the dinuclear species $[Cu_2L_2Cl(OH)Na]^+$. After the addition of triethylamine to **2**, the spectrum shows a base peak at *m*/*z* 102.1 (100%) due to the presence of the cationic species $[Et_3NH]^+$. A new peak generated at *m*/*z* 662.81 indicates the presence of the dinuclear species $[Cu_2L_2Cl(OH)(H_2O)Na]^+$. After the addition of 3,5-DTBC to the solutions of the complexes, some new peaks are generated. In both cases, the spectra exhibit a base peak at *m*/*z* 243 (100%) corresponding to the quinone sodium aggregate [3,5-DTBQ-Na]$^+$. The peaks at *m*/*z* 506.2 and 789.0 corroborate the formation of species [CuL(3,5-DTBC)H]$^+$ and $[Cu_2L_2$(3,5-DTBC)]$^+$, respectively. It is interesting to note that the mass spectra of **1** and **2** are essentially the same after the addition of 3,5-DTBC. Hence, one may infer that the differences in the catecholase activities of **1** and **2** might be caused simply by the presence of 1 equiv of base in methanol solutions of **2** (originating from the hydroxido bridge), while the copper species are essentially identical.

Electrochemistry. The electrochemical properties of both complexes have been investigated to correlate the redox properties of the copper(II) complexes with their catecholase activity. The redox potential should be such as to permit the reoxidation of the reduced copper centers by molecular oxygen to maintain the catalytic cycle. The cyclic voltammograms in a acetonitrile solution of both complexes display irreversible cathodic responses, and the electrochemical data are summarized in Table S2 in the Supporting Information. The reduction peaks are tentatively assigned to the one-electron processes $Cu^{II}Cu^{II} \rightarrow Cu^{II}Cu^{I}$ and $Cu^{II}Cu^{I} \rightarrow Cu^{I}Cu^{I}$. During the anodic potential scan, both complexes show an oxidative response at ca. −0.11 V with a very narrow width and high peak current (Figure S21 in the Supporting Information). The response at −0.11 V is typical of the anodic stripping of copper and has also been observed in similar complexes.[2c] Thus, the electrochemical behavior of complexes **1** and **2** is very similar, indicating the presence of similar species in solution under these conditions.

■ CONCLUSIONS

The tridentate reduced Schiff base ligand HL {2-[[2-(diethylamino)ethylamino]methyl]phenol} upon reaction with copper(II) perchlorate afforded a phenoxido-bridged dicopper complex, **1**. The addition of triethylamine in a methanol solution of this complex transformed it into a novel double phenoxido- and single hydroxido-bridged dinuclear copper(II) complex, **2**. The additional hydroxido bridge shifted the two equatorial−equatorial phenoxido bridges to axial−equatorial positions and itself occupied the equatorial−equatorial position. In **2**, this triple-bridging arrangement brings the two copper atoms in closer proximity and the magnetic coupling drastically changes from strong antiferromagnetic to ferromagnetic. This behavior can be explained by considering equatorial−equatorial bridging angles of average 100.75° (phenoxido) in **1** and average 93.10° (hydroxido) in **2**, which are the effective pathways for magnetic coupling. To the best of our knowledge, complex **2** is the first ferromagnetic dinuclear copper(II) complex in which magnetic coupling takes place through a single hydroxido bridge. The higher catecholase activity of complex **2** compared to **1** is rather unexpected considering the Cu−Cu distances in the solid-state structures. However, both of the species generate essentially identical species in solution except that the pH of the solution of **2** is higher because the OH group produces 1 equiv of base in its solution. This higher pH facilitates deprotonation of catechol and, consequently, its coordination to the metal centers. Hence, the catecholase activity of complex **2** is higher.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format for the structures reported and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ghosh_59@yahoo.com.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank CSIR, Government of India [Senior Research Fellowship to A.B., Sanction No. 09/028(0717)/2008-EMR-I, and Junior Research Fellowship to L.K.D., Sanction No. 09/028(0805)/2010-EMR-I], and DST FIST for financial support for the X-ray diffraction facility. We also thank the British Engineering and Physical Sciences Research Council and the University of Reading for funds for the X-Calibur system and the Spanish Government (Grant CTQ2009-07264) for financial support.

■ REFERENCES

(1) (a) Venegas-Yazigia, D.; Aravena, D.; Spodine, E.; Ruiz, E.; Alvarez, S. *Coord. Chem. Rev.* **2010**, *254*, 2086. (b) Stylianou, M.; Drouza, C.; Viskadourakis, Z.; Giapintzakis, J.; Keramidas, A. D. *Dalton Trans.* **2008**, 6188. (c) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *Inorg. Chem.* **1997**, *36*, 3683. (d) Youngme, S.; van Albada, G. A.; Roubeau, O.; Chaichit, C. N.; Reedijk, J. *Inorg. Chim. Acta* **2003**, *342*, 48. (e) Chou, C.-C.; Su, C.-C.; Tsai, H.-L.; Lii, K.-H. *Inorg. Chem.* **2005**, *44*, 628. (f) Melnik, M. *Coord. Chem. Rev.* **1982**, *42*, 259. (g) Koval, I. A.; van der Schilden, K.; Schuitema, A. M.; Gamez, P.; Belle, C.; Pierre, J.-L.; Lulken, M.; Krebs, B.; Roubeau, O.; Reedijk, J. *Inorg. Chem.* **2005**, *44*, 4372. (h) Biswas, A.; Drew, M. G. B.; Ribas, J.; Diaz, C.; Ghosh, A. *Eur. J. Inorg. Chem.* **2011**, 2405. (i) Biswas, A.; Drew, M. G. B.; Song, Y.; Ghosh, A. *Inorg. Chim. Acta* **2011**, *376*, 422. (j) Biswas, A.; Drew, M. G. B.; Ribas, J.; Diaz, C.; Ghosh, A. *Inorg. Chim. Acta* **2011**, *379*, 28.

(2) (a) Koval, I. A.; Gamez, P.; Belle, C.; Selmeczi, K.; Reedijk, J. *Chem. Soc. Rev.* **2006**, *35*, 814 and references cited therein. (b) Sreenivasulu, B.; Vetrichelvan, M.; Zhao, F.; Gao, S.; Vittal, J. J. *Eur. J. Inorg. Chem.* **2005**, 4635. (c) Neves, A.; Rossi, L. M.; Bortoluzzi, A. J.; Szpoganicz, B.; Wiezbicki, C.; Schwingel, E.; Haase, W.; Ostrovsky, S. *Inorg. Chem.* **2002**, *41*, 1788. (d) Rey, N. A.; Neves, A.; Bortoluzzi, A. J.; Pich, C. T.; Terenzi, H. *Inorg. Chem.* **2007**, *46*, 348. (e) Bhardwaj, V. K.; Aliaga-Alcalde, N.; Corbella, M.; Hundal, G. *Inorg. Chim. Acta* **2010**, *363*, 97. (f) Koval, I. A.; Selmeczi, K.; Belle, C.; Philouze, C.; Saint-Aman, E.; Gautier- Luneau, I.; Schuitema, A. M.; Vliet, M. v.; Gamez, P.; Roubeau, O.; Luken, M.; Krebs, B.; Lutz, M.; Spek, A. L.; Pierre, J.-L.; Reedijk, J. *Chem.—Eur. J.* **2006**, *12*, 6138. (g) Osório, R. E. H. M. B.; Peralta, R. A.; Bortoluzzi, A. J.; deAlmeida, V. R.; Szpoganicz, B.; Fischer, F. L.; Terenzi, H.; Mangrich, A. S.; Mantovani, K. M.; Ferreira, D. E. C.; Rocha, W. R.; Haase, W.; Tomkowicz, Z.; dos Anjos, A.; Neves, A. *Inorg. Chem.* **2012**, *51*, 1569. (h) Mijangos, E.; Reedijk, J.; Gasque, L. *Dalton Trans.* **2008**, 1857.

(3) (a) Chaudhuri, P.; Wagner, R.; Weyhermuller, T. *Inorg. Chem.* **2007**, *46*, 5134. (b) Kruse, T.; Weyhermuller, T.; Wieghardt, K. *Inorg. Chim. Acta* **2002**, *331*, 81.

(4) (a) van Albada, G. A.; Mutikainen, I.; Turpeinen, U.; Reedijk, J. *Inorg. Chim. Acta* **2001**, *324*, 273. (b) Zheng, Y. Q.; Cheng, D. Y.; Liu, B. B.; Huang, W. X. *Dalton Trans.* **2011**, *40*, 277. (c) McGregor, K. T.; Watkins, N. T.; Lewis, D. L.; Drake, R. F.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 423. (d) Castro, I.; Faus, J.; Julve, M.; Verdaguer, M.; Monge, A.; Gutierrez-Puebla, E. *Inorg. Chim. Acta* **1990**, *170*, 251. (e) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.

(5) (a) Das, K.; Mandal, T. N.; Roy, S.; Jana, A.; Konar, S.; Lui, C. M.; Barik, A. K.; Kar, S. K. *Polyhedron* **2011**, *30*, 715. (b) Li, X.; Cheng, D.; Lin, J.; Li, Z.; Zheng, Y. *Cryst. Growth Des.* **2008**, *8*, 2853. (c) De Munno, G.; Julve, M.; Lloret, F.; Faus, J.; Verdaguer, M.; Caneschi, A. *Inorg. Chem.* **1995**, *34*, 157. (d) Castro, I.; Julve, M.; De Munno, G.; Bruno, G.; Real, J. A.; Lloret, F.; Faus, J. *J. Chem. Soc., Dalton Trans.* **1992**, 1739. (e) Manzur, J.; Mora, H.; Vega, A.; Spodine, E.; Venegas-Yazigi, D.; Garland, M. T.; El Fallah, M. S.; Escuer, A. *Inorg. Chem.* **2007**, *46*, 6924. (f) Safei, E.; Wojtczak, A.; Bill, E.; Hamidi, H. *Polyhedron* **2010**, *29*, 2769. (g) Safei, E.; Rasouli, M.; Weyhermüller, T.; Bill, E. *Inorg. Chim. Acta* **2011**, *375*, 158.

(6) Rompel, A.; Fischer, H.; Meiwes, D.; Buldt-Karentzopoulos, K.; Dillinger, R.; Tuczek, F.; Witzel, H.; Krebs, B. *J. Biol. Inorg. Chem.* **1999**, *4*, 56.

(7) Oishi, N.; Nishida, Y.; Ida, K.; Kida, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2847.

(8) (a) Ackermann, J.; Meyer, F.; Kaifer, E.; Pritzkow, H. *Chem.—Eur. J.* **2002**, *8*, 247. (b) Mukherjee, J.; Mukherjee, R. *Inorg. Chim. Acta* **2002**, *337*, 429. (c) Torelli, S.; Belle, C.; Gautier-Luneau, I.; Pierre, J. L.; Saint-Aman, E.; Latour, J. M.; Le Pape, L.; Luneau, D. *Inorg. Chem.* **2000**, *39*, 3526. (d) Peralta, R. A.; Bortoluzzi, A. J.; Szpoganicz, B.; Brandaoa, T. A. S.; Castellano, E. E.; de Oliveira, M. B.; Severino, P. C.; Terenzi, H.; Neves, A. *J. Phys. Org. Chem.* **2010**, *23*, 1000.

(9) (a) Zippel, F.; Ahlers, F.; Werner, R.; Haase, W.; Nolting, H.-F.; Krebs, B. *Inorg. Chem.* **1996**, *35*, 3409. (b) Kao, C.-H.; Wei, H.-H.; Liu, Y.-H.; Lee, G.-H.; Wang, Y.; lee, C.-J. *J. Inorg. Biochem.* **2001**, *84*, 171. (c) Wegner, R.; Gottschaldt, M.; Gorls, H.; Jager, E.-G.; Klemm, D. *Chem.—Eur. J.* **2001**, *7*, 2143.

(10) (a) Merkel, M.; Moller, N.; Piacenza, M.; Grimme, S.; Rompel, A.; Krebs, B. *Chem.—Eur. J.* **2005**, *11*, 1201. (b) Fernandes, C.; Neves, A.; Bortoluzzi, A. J.; Mangrich, A. S.; Rentschler, E.; Szpoganicz, B.; Schwingel, E. *Inorg. Chim. Acta* **2001**, *320*, 12.

(11) (a) Koval, I. A.; Huisman, M.; Stassen, A. F.; Gamez, P.; Roubeau, O.; Belle, C.; Pierre, J. L.; Saint-Aman, E.; Luken, M.; Krebs, B.; Lutz, M.; Spek, A. L.; Reedijk, J. *Eur. J. Inorg. Chem.* **2004**, 4036. (b) Gentschev, P.; Feldmann, A. A.; Luken, M.; Moller, N.; Sirges, H.; Krebs, B. *Inorg. Chem. Commun.* **2002**, *5*, 64.

(12) Kodera, M.; Kawata, T.; Kano, K.; Tachi, Y.; Itoh, S.; Kojo, S. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1957.

(13) Monzani, E.; Quinti, L.; Perotti, A.; Casella, L.; Gulotti, M.; Randaccio, L.; Geremia, S.; Nardin, G.; Faleschini, P.; Tabbi, G. *Inorg. Chem.* **1998**, *37*, 553.

(14) Mendoza-Quijano, M. R.; Ferrer-Sueta, G.; Flores-Álamo, M.; Aliaga-Alcalde, N.; Gómez-Vidales, V.; Ugalde-Saldívara, V. M.; Gasque, L. *Dalton Trans.* **2012**, *41*, 4985.

(15) Biswas, A.; Drew, M. G. B.; Gómez-García, C. J.; Ghosh, A. *Inorg. Chem.* **2010**, *49*, 8155.

(16) (a) Biswas, A.; Drew, M. G. B.; Ghosh, A. *Polyhedron* **2010**, *29*, 1029. (b) Biswas, A.; Saha, R.; Ghosh, A. *CrystEngComm* **2011**, *13*, 5342.

(17) *CrysAlis*; Oxford Diffraction Ltd.: Abingdon, U.K., 2006.

(18) *SHELXS97 and SHELXL97, Programs for Crystallographic Solution and Refinement*: Sheldrick., G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

(19) *ABSPACK: Program for Absorption Corrections*; Oxford Diffraction: Abingdon, U.K., 2007.

(20) (a) Ray, M. S.; Mukhopadhyay, G.; Drew, M. G. B.; Lu, T.-H.; Chaudhuri, S.; Ghosh, A. *Inorg. Chem. Commun.* **2003**, *6*, 961. (b) Wichmann, O.; Sopo, H.; Colacio, E.; Mota, A. J.; Sillanpää. *Eur. J. Inorg. Chem.* **2009**, 4877.

(21) (a) Biswas, C.; Drew, M. G. B.; Figuerola, A.; Gómez-Coca, S.; Ruiz, E.; Tangoulis, V.; Ghosh, A. *Inorg. Chim. Acta* **2010**, *363*, 846. (b) Bian, H. D.; Xu, J. Y.; Gu, W.; Yan, S. P.; Cheng, P.; Liao, D. Z.; Jiang, Z. H. *Polyhedron* **2003**, *22*, 2927. (c) Sarkar, B.; Ray, M. S.; Li, Y.-Z.; Song, Y.; Figuerola, A.; Ruiz, E.; Cirera, J.; Cano, J.; Ghosh, A. *Chem.—Eur. J.* **2007**, *13*, 9297. (d) Mukherjee, P.; Drew, M. G. B.; Estrader, M.; Diaz, C.; Ghosh, A. *Inorg. Chim. Acta* **2008**, *361*, 161.

(22) Mukherjee, P.; Drew, M. G. B.; Gómez-García, C. J.; Ghosh, A. *Inorg. Chem.* **2009**, *48*, 5848.

(23) Addison, A. W.; Rao, T. N.; Reedijk, J.; Van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

(24) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.

(25) (a) Venegas-Yazigi, D.; Cortes, S.; Paredes-Garcia, V.; Pena, O.; Ibaneza, A.; Baggio, R.; Spodine, E. *Polyhedron* **2006**, *25*, 2072. (b) Korupoju, S. R.; Mangayarkarasi, N.; Ameerunisha, S.; Valente, E. J.; Zacharias, P. S. *J. Chem. Soc., Dalton Trans.* **2000**, 2845. (c) Chu, Z.; Huang, W.; Wang, L.; Gou, S. *Polyhedron* **2008**, *27*, 1079. (d) Mandal,

S. K.; Thompson, L. K.; Newlands, M. J.; Gabe, E. J. *Inorg. Chem.* **1989**, *28*, 3707. (e) Gentschev, P.; Moller, N.; Krebs, B. *Inorg. Chim. Acta* **2000**, *300*, 442. (f) Brychcy, K.; Drager, K.; Jens, K.-J.; Tilset, M.; Behrens, U. *Chem. Ber.* **1994**, *127*, 465. (g) Assey, G. E.; Yisgedu, T.; Gultneh, Y.; Butcher, R. J.; Tesema, Y. *Acta Crystallogr.* **2009**, *E65*, m1007. (h) Panther, T.; Behrens, U. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1934. (i) Sekine, N.; Shiga, T.; Ohba, M.; Okawa, H. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 881.

(26) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

(27) (a) Patra, A. K.; Ray, M.; Mukherjee, R. *Polyhedron* **2000**, *19*, 1423. (b) Haddad, M. S.; Wilson, S. R.; Hodgson, D. J.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1981**, *103*, 384. (c) Adams, H.; Bailey, N. A.; Collinson, S. R.; Fenton, D. E.; Haring, C. J.; Kitchen, S. J. *Inorg. Chim. Acta* **1996**, *246*, 81. (d) Coughlin, P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 3228. (e) Lu, Q.; Latour, J.-M.; Harding, C. J.; Martin, N.; Marrs, D. J.; McKee, V.; Nelson, J. *J. Chem. Soc., Dalton Trans.* **1994**, 1471. (f) Harding, C. J.; McKee, V.; Nelson, J.; Lu, Q. *J. Chem. Soc., Chem. Commun.* **1993**, 1768. (g) Spodine, E.; Manzur, J.; Garland, M. T.; Kiwi, M.; Pena, O.; Grandjean, D.; Poupet, L. *J. Chem. Soc., Dalton Trans.* **1991**, 365. (h) Drew, M. G. B.; McCann, M.; Martin-Nelson, M. *J. Chem. Soc., Dalton Trans.* **1981**, 1868. (i) Castro, I.; Faus, J.; Julve, M.; Lloret, F.; Verdaguer, M.; Kahn, O.; Jeannin, S.; Jeannin, Y.; Vaisserman, J. *J. Chem. Soc., Dalton Trans.* **1990**, 2207. (j) Foldago, J. V.; Coronado, E.; Beltran-Porter, D.; Rojo, T.; Fuertes, J. *J. Chem. Soc., Dalton Trans.* **1989**, 237. (k) Harding, C. J.; Lu, Q.; Malone, J. F.; Marrs, D. J.; Martin, N.; McKee, V.; Nelson, J. *J. Chem. Soc., Dalton Trans.* **1995**, 1739.

(28) Banu, K. S.; Chattopadhyay, T.; Banerjee, A.; Mukherjee, M.; Bhattacharya, S.; Patra, G. K.; Zangrando, E.; Das, D. *Dalton Trans.* **2009**, 8755.

(29) Reim, J.; Krebs, B. *J. Chem. Soc., Dalton Trans.* **1997**, 3793.