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Azido bridge mediated catecholase activity, electrochemistry and magnetic behavior of a dinuclear copper(II) complex of a phenol based "end-off" compartmental ligand

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ABSTRACT

A dinuclear Cu(II) species $[Cu_2L_2(H_2O)_2(N_3)](NO_3)_2$ (L = 2,6-bis(*N*-ethylpyrrolidine-iminomethyl)-4-methyl-phenolato) where two Cu centers are bridged by phenoxido and $\mu_{1,1}$-azido bridges with Cu–Cu separation of ~3 Å have been synthesized with the view to explore the role of azido bridge on catecholase activity and electrochemical property and the roles of both the bridging groups on magnetic coupling of two copper centers. The complex exhibits excellent catecholase activity in acetonitrile as well as in DMSO medium not only by oxidizing 3,5-di-*tert*-butylcatechol (3,5-DTBC) but also tetrachlorocatechol (TCC), a catechol which is very thorny to oxidize, under aerobic conditions and becomes the first example of its own kind. CV study reveals three quasi-reversible reductive couples which are tentatively assigned as Cu^{II}_2 to $Cu^{II}Cu^{I}$ and $Cu^{I}Cu^{I}$ reduction followed by reduction of $Cu^{I}Cu^{I}$ complex to $Cu^{0}Cu^{0}$ species. Variable temperature magnetic study suggests the presence of an antiferromagnetic spin–exchange interaction between Cu(II) ions in the dimer via double bridge where the antiferromagnetic contribution of phenoxido bridge predominates over the ferromagnetic interaction of azido bridge.

1. Introduction

Dinuclear copper complexes with Cu–Cu separation of ~3 Å are interesting as corroborative model of the active site of catechol oxidase to elucidate the functional mechanism of the native enzyme and to develop bio-inspired catalytic systems [1–9]. When that separation is associated with bridging azido ligand the species becomes of particularly interesting for gaining deeper insight into magneto-structural correlation, a study very much essential for developing new functional molecule based materials [10–14]. The intense study on synthetic analogs of active site of catechol oxidase in last decade reveals that successful models must possess some characteristic structural features and one of the most important features is the presence of hydroxo bridge as is noticed in the crystal structure of the active site of the native enzyme in the met state [6–9]. We were in search whether any other bridging entity may exert the similar effect as of hydroxo bridge. We are successful in our search when we worked with an "end-off" compartmental ligand selecting azide as the bridging entity. The selection of an "end-off" compartmental ligand is to full fill the basic requirement of keeping two copper atoms in the optimum distance of ~3 Å and that of azide is just to exploit its versatile coordination modes. It is obvious that azide either in $\mu_{1,3}$ or $\mu_{1,1}$ mode may act as bridging ligand [10,11]. The azido bridge is generally antiferromagnetic for the $\mu_{1,3}$-N_3 (end-to-end, EE) mode, though, in the recent past, some exceptions have been reported [15–18]. For the $\mu_{1,1}$-N_3 (end-on, EO) bridging mode, ferromagnetic ordering is established when the Cu–N–Cu angle is small, which has been attributed to a spin-polarization effect [19–22]. We are reporting herein synthesis, structural characterization of $[Cu_2L_2(H_2O)_2(\mu_{1,1}\text{-}N_3)](NO_3)_2$ (L = 2,6-bis(*N*-ethylpyrrolidine-iminomethyl)-4-methyl-phenolato), catecholase activity in DMSO and acetonitrile medium using 3,5-di-*tert*-butylcatechol (3,5-DTBC) and tetrachlorocatechol (TCC) as substrate, electrochemistry and variable temperate magnetic study and magneto-structural correlations.

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2. Experimental section

2.1. Physical methods and materials

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer and copper content was estimated gravimetrically. Infrared spectra were recorded on KBr disks (400–4000 cm^{-1}) with a Perkin–Elmer RXI FTIR spectrophotometer. Electronic spectra (200–800 nm) were measured at room temperature on a Shimadzu UV-3101PC by using dry methanol/DMSO as medium. Cyclic voltammetric and DPV measurements were performed by using a CH1106A potentiostat with glassy carbon (GC) as working electrode, Pt-wire as counter electrode and Ag, AgCl/sat KCl as reference electrode. Magnetic susceptibility measurements over the temperature range 5–300 K was performed at a magnetic field of 0.0750 T using a MPMS SQUID-VSM dc magnetometer. Correction for the sample holder, as well as the diamagnetic correction, which was estimated from the Pascal constants, [23] was applied.

All solutions were purged with dinitrogen prior to measurements. All other chemicals used in this study were obtained from commercial sources and used as received. Solvents were dried according to standard procedure and distilled prior to use. 4-Methyl-2,6-diformylphenol was prepared according to the literature method [24]. *N*-(2-Aminoethyl)pyrrolidine was purchased from Sigma–Aldrich Chemical Company and used as received.

2.2. Synthesis of the complex

2.2.1. $[Cu_2(L)(H_2O)_2(N_3)](NO_3)_2$ (**1**)

A methanolic solution (5 mL) of *N*-(2-aminoethyl)pyrrolidine (0.256 g, 2 mmol) was added dropwise to a heated methanolic solution (10 mL) of 4-methyl-2,6-diformylphenol (0.164 g, 1 mmol), and the resulting mixture was refluxed for half an hour. Then, a methanolic solution (15 mL) of $Cu(NO_3)_2{\cdot}3H_2O$ (0.604 g, 2.5 mmol) was added to it and the reflux was further continued for 2 h. After cooling down the reaction mixture at room temperature a water–methanolic (1:1) solution (5 mL) of sodium azide (0.325 g, 5 mmol) was added dropwise at stirring condition. The resulting mixture was allowed to stir for 3 h and filtered. After filtration, the clear deep-green solution was kept in a $CaCl_2$ desiccators in dark. Square-shaped deep-green crystals, suitable for X-ray analysis, were obtained from the filtrate after a few days (yield 70%). *Anal.* Calc. for $C_{21}H_{35}Cu_2N_9O_9$: C, 36.84; H, 5.15; N, 18.41; Found: C, 36.94; H, 4.89; N, 18.47%; IR: ν(C=N) 1653 cm^{-1}; ν (skeletal vibration) 1553 cm^{-1}; $\nu(H_2O)$ 3434 cm^{-1}; $\nu(N_3^{-1})$ 2079 cm^{-1}.

2.3. X-ray data collection and crystal structure determination

The single crystal of complex **1** was mounted on a glass fiber and coated with epoxy resin. Intensities data were collected at room temperature on a Nonius DIP-1030H system with Mo Kα radiation (λ = 0.71073 Å). Maximum diffraction angle theta was 24.7° (completeness of 96%) due to poor diffracting crystals. Cell refinement, indexing and scaling of the data sets were carried out using Denzo and Scalepack [25]. The structure was solved by direct methods and subsequent Fourier analyses [26] and refined by the full-matrix least-squares method based on F^2 with all observed reflections using SHELX-97 [26] software. The non-hydrogen atoms were refined anisotropically. All calculations were carried out using WINGX System version 1.80.05 [27].

The CCDC number of the complex is 1033058. Pertinent crystallographic data and refinement details are summarized in Table 1.

Table 1
Crystallographic data and details of refinements for complex **1**.

Empirical formula	$C_{21}H_{35}Cu_2N_9O_9$	$F(000)$	1416
Formula weight	684.66	θ_{max} (°)	24.71
Crystal system	monoclinic	Reflections collected	8822
Space group	$P2_1/n$	Unique reflections	4687
a (Å)	8.8950(11)	R_{int}	0.044
b (Å)	17.1010(13)	Observed $I > 2\sigma(I)$	2733
c (Å)	19.0790(19)	Parameters	383
β (°)	97.475(10)	Goodness of fit (F^2)	0.917
V (Å^3)	2877.5(5)	R_1 ($I > 2\sigma(I)$)	0.0498
Z	4	wR_2	0.1298
D_{calc} (mg m^{-3})	1.542	$\Delta\rho$ (e Å^3)	−0.545, 0.372

3. Results and discussion

3.1. Synthesis and characterization

The complex was synthesized adopting template synthesis technique in which a methanolic solution of copper(II) nitrate trihydrate was treated with the Schiff-base formed *in situ* by the reaction between 4-methyl-2,6-diformylphenol and *N*-(2-aminoethyl) pyrrolidine. Complex **1** was obtained after the addition of a water–methanolic solution of sodium azide (four times with respect to the copper salt). The IR spectrum of the complex shows a band due to C=N stretch at 1646 cm^{-1} and skeletal vibration at 1553 cm^{-1}. Broad band centered at 1383 cm^{-1} indicates the presence of weakly coordinated nitrate ion in the complex. A strong band observed at 2079 cm^{-1} confirms the presence of bridging azide ion in the complex (see Table 2).

3.2. Description of crystal structure

The structural analysis of compound **1** shows that it comprises of a dicationic species $[Cu_2L(H_2O)_2(N_3)]^{2+}$ counterbalanced by two nitrate anions. The ORTEP drawing of the complex is shown in Fig. 1, while a selection of coordination geometry parameters is reported in Table 3. The metals are chelated by the ligand L through the phenoxido oxygen, the imino and amino pyrrolidine nitrogen donors, and bridged by a $\mu_{1,1}$ azide, completing their square pyramidal coordination sphere through aqua ligands. The Cu–O(phenoxo) bond lengths are comparable being of 1.982(3) and 1.960(3) Å for Cu1 and Cu2, respectively. The length of the Cu–N(imino) bond distances (1.924(4) and 1.916(5) Å) are similar to those involving the bridging azide (1.983(4) and 1.998(5) Å). On the other hand the Cu–N(pyrrolidine) ones are slightly longer, of 2.037(4) and 2.028(4) Å, for the different hybridization of N atom donors. On the other hand the water molecules at apical

Table 2
Coordination bond lengths (Å) and angles (°) for complex **1**.

Cu(1)–N(1)	1.924(4)	Cu(2)–N(3)	1.916(5)
Cu(1)–N(2)	2.037(4)	Cu(2)–N(4)	2.028(4)
Cu(1)–O(1)	1.982(3)	Cu(2)–O(1)	1.960(3)
Cu(1)–N(5)	1.983(4)	Cu(2)–N(5)	1.998(5)
Cu(1)–O(1w)	2.330(4)	Cu(2)–O(2w)	2.337(5)
Cu(1)–O(8)	2.753(5)	Cu(2)–O(4)	2.979(6)
N(1)–Cu(1)–N(2)	86.0(2)	N(3)–Cu(2)–N(4)	86.0(2)
N(1)–Cu(1)–O(1)	91.4(2)	N(3)–Cu(2)–O(1)	91.6(2)
N(1)–Cu(1)–N(5)	167.0(2)	N(3)–Cu(2)–N(5)	169.2(2)
N(1)–Cu(1)–O(1w)	95.8(2)	N(3)–Cu(2)–O(2w)	96.4(2)
N(2)–Cu(1)–O(1)	176.5(2)	N(4)–Cu(2)–O(1)	168.5(2)
N(2)–Cu(1)–N(5)	103.4(2)	N(4)–Cu(2)–N(5)	102.3(2)
N(2)–Cu(1)–O(1w)	94.1(2)	N(4)–Cu(2)–O(2w)	96.3(2)
O(1)–Cu(1)–N(5)	78.8(2)	O(1)–Cu(2)–N(5)	78.9(2)
O(1)–Cu(1)–O(1w)	88.6(2)	O(1)–Cu(2)–O(2w)	95.1(2)
N(5)–Cu(1)–O(1w)	92.5(2)	N(5)–Cu(2)–O(2w)	89.5(2)
Cu(1)–O(1)–Cu(2)	101.8(2)	Cu(1)–N(5)–Cu(2)	100.5(2)

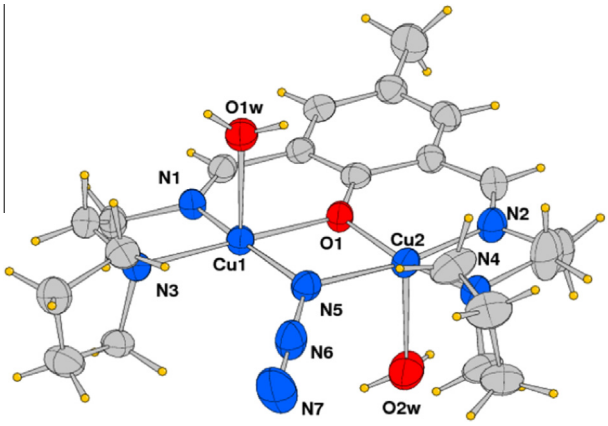

Fig. 1. ORTEP drawing of complex cation of **1** (30% ellipsoid probability).

position of the square pyramidal coordination geometry are at sensibly longer distance (Cu1–OH_2 = 2.330(4) and Cu2–OH_2 = 2.337(5) Å). The bridging Cu(1)–O(1)–Cu(2) and Cu(1)–N(5)–Cu(2) bond angles are of 101.83(16)° and 100.5(2)°, respectively, leading to a metal–metal separation of 3.0604(9) Å. The intermetallic distance is *ca.* 0.1 Å longer than the values of 2.918(2) and 2.9450(4) Å measured in the correspondent complexes $[Cu_2(L')(OH)(H_2O)(NO_3)_2]$ where the phenol is a 4-chloro- or 4-*tert*-butyl derivative, respectively, and metals are bridged by a hydroxyl OH group rather than the azide [2]. It is worth of note the crystal packing showing nitrate anions H-bond connected by the coordinated water molecules so that to form a polymeric chain elongated along axis *a* (Fig. 2, range of Ow...O distances 2.736(8)–2.848(8) Å). The supramolecular motif generated from the intermolecular H-bonds can be designated as a $R_4^2(12)$ synthon [28]. The position of nitrate anions is such that an oxygen is located at 2.753(5) and 2.979(6) Å from copper Cu1 and Cu2, respectively. These long distances indicate a possible weak interaction of nitrate with copper ions, also confirmed by the slight displacement of metals by *ca.* 0.10 and 0.15 Å from the mean basal plane towards these species.

3.3. Catecholase activity

Catechol oxidase, a type-3 copper protein can binds oxygen reversibly at room temperature and so it can be utilized to oxidize phenols to respective o-benzoquinones. As a model of the enzyme we have taken one dinuclear azido bridged complex of Cu(II) and study it's efficiency towards oxidation of 3,5-DTBC to 3,5-DTBQ and TCC to TCQ, respectively. Interestingly, it displays significant catalytic activity towards the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) to 3,5-di-*tert*-butylbenzoquinone (3,5-DTBQ) and tetrachlorocatechol (TCC) to tetrachloroquinone (TCQ) in DMSO as well as in acetonitrile medium. Before proceeding into detailed kinetic study we have checked the ability of our complex to mimic the active site of catechol oxidase by treating 1×10^{-4} mol dm^{-3} solutions of complex **1** with 1×10^{-2} mol dm^{-3} (100 equivalents) of 3,5-DTBC and TCC under aerobic condition. The course of the reaction was followed by UV–Vis spectroscopy (Fig. 3). The time dependent UV–Vis spectral scan was performed in pure acetonitrile and DMSO medium. The complex shows a smooth conversion of 3,5-DTBC to 3,5-DTBQ in both solvent. It is also able to convert TCC to TCQ which is hard to oxidize under ordinary condition. Fig. 3 (a) and (b) show the spectral change for our complex upon addition of 100-fold 3,5-DTBC (1×10^{-2} M) observed at interval of 5 min in DMSO medium. The kinetics of the 3,5-DTBC and TCC oxidation was determined by monitoring the increase of the concentration of the product 3,5-DTBQ and TCQ. The experimental conditions were the same as we reported earlier [1]. The complex showed saturation kinetics and a treatment based on the Michaelis–Menten model seemed to be appropriate. The binding constant (K_M), maximum velocity (V_{max}), and rate constant for dissociation of substrates (i.e., turnover number, k_{cat}) were calculated by using the Lineweaver–Burk graph of $1/V$ versus $1/[S]$ (Figs. S2–S5 and S8–S11), using the equation $1/V = \{K_M/V_{max}\}\{1/[S]\} + 1/V_{max}$, and the kinetic parameters are presented in Tables S1–S2 in SI file.

Here the activity of the complex is higher in acetonitrile medium than in DMSO medium. It can be explained by considering the higher coordinating ability of the solvent which retarded the possibility of catechol–substrate adduct formation.

In one of our earlier study [1] we reported the catecholase activity of a similar hydroxo-bridged complex in acetonitrile and

Table 3
Geometrical parameters (Å/°) for H bonds.

Donor–H	A	D–H	H...A	D...A	D–H...A	Symmetry code of A
O(1w)–H(1a)	O(4)	0.83(6)	1.98(6)	2.789(8)	164(8)	–
O(1w)–H(1b)	O(7)	0.85(6)	2.05(6)	2.848(8)	156(8)	1 + *x*, *y*, *z*
O(2w)–H(2a)	O(8)	0.85(4)	2.12(7)	2.817(9)	140(7)	–
O(2w)–H(2b)	O(6)	0.84(7)	2.32(8)	2.736(8)	111(8)	−1 + *x*, *y*, *z*

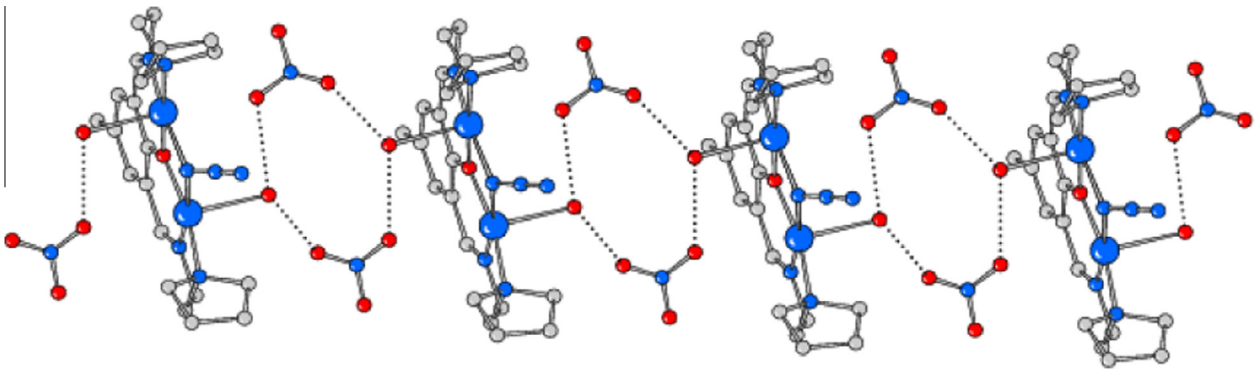

Fig. 2. Polymeric chain elongated along axis a built by H bond formed between aqua ligands and nitrate anions (H atoms not shown for sake of clarity).

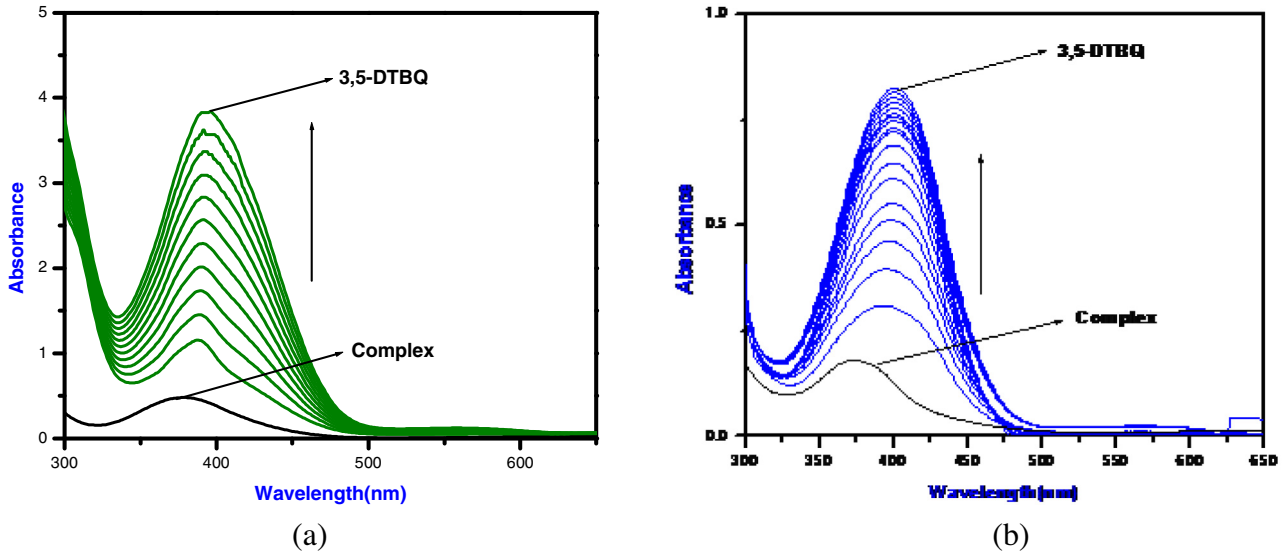

Fig. 3. Changes observed in UV–Vis spectra of complex (1×10^{-4} M) (a) in acetonitrile and (b) in DMSO medium upon addition of 100-fold 3,5-DTBC (1×10^{-2} M).

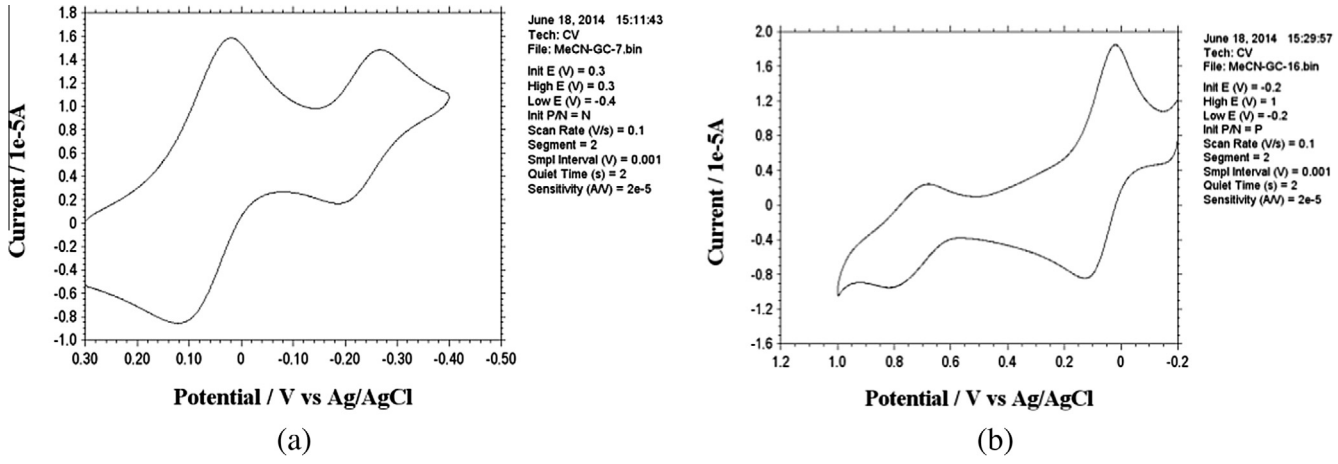

Fig. 4. CV spectrum of complex **1** (a) in negative potential, (b) positive potential, at the GC electrode at 100 mV s^{-1} scan rate.

methanol medium where the complex forms an adduct with 3,5-DTBC in acetonitrile medium and was unable to oxidize TCC to TCQ. But our newly synthesized azido-bridged complex is being able to oxidize 3,5-DTBC to 3,5-DTBQ as well as TCC to TCQ, respectively in both acetonitrile and DMSO medium. To the best of our knowledge this is the first azido bridged complex which is able to oxidize TCC to TCQ both in acetonitrile and in DMSO medium.

*3.3.1. Mechanistic interpretation on catecholase activity exhibited by complex **1***

The reports so far available on mechanism of catecholase activity of the synthetic analogs of catechol oxidase reveal that the very first step of the mechanism is the substrate–copper center(s) interaction. Coordination of catechol may be monodentate asymmetric type, bridging bidentate or combination of both. In our present case the spectral study is not distinct enough to assign the binding mode of catechol to the copper center as we noticed in our earlier studies. However, a pre-equilibrium of the free complex and the substrate prior to the intramolecular electron transfer is a key step of the mechanism which follows reduction of Cu(II) to Cu(I) with concomitant oxidation of catechol to quinone. Now the rate determining step may be either the re-oxidation of copper(I) by dioxygen or the intramolecular electron transfer. Since in our case the d–d band remains intact with slight blue shift (Fig. S12) during the catalytic reaction the intramolecular electron transfer is most probably the rate determining step. The role of dioxygen is very crucial for regeneration of the catalyst with its concomitant reduction of either kind: (i) two electron reduction to H_2O_2 or (ii) four electron reduction to water. Our spectral study after treating with iodide fails to detect I^{3-} (Fig. S13) and thereby clearly eliminate the possibility of dioxygen reduction to H_2O_2 in our case.

3.4. Cyclic voltammetric study

The electron transfer behavior of the complex was investigated by cyclic voltammetry at a GC electrode in MeCN solution. The binuclear Cu(II) complex shows three quasi-reversible reductive couples (Fig. 4) at 0.06 V (92 mV), −0.26 V (76 mV) and −0.55 V (115 mV), the last couple showing cathodic peak current value which is almost twice that of the first couple. We tentatively assign the first two couples to successive one electron reductions of the Cu_2^{II} to $Cu^{II}Cu^{I}$ and $Cu^{I}Cu^{I}$ species, whereas the couple at −0.55 V is assigned to reduction of $Cu^{I}Cu^{I}$ complex to $Cu^{0}Cu^{0}$ species. At more negative potentials, at −1.12 V and −1.78 V, ligand based

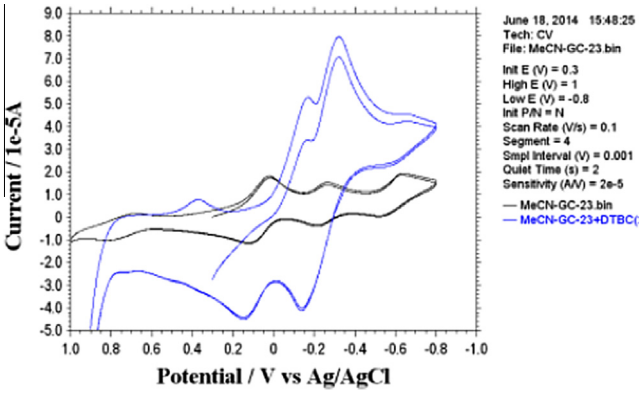

Fig. 5. CV spectrum of complex **1** in presence of 3,5-DTBC at the GC electrode at 100 mV s^{-1} scan rate.

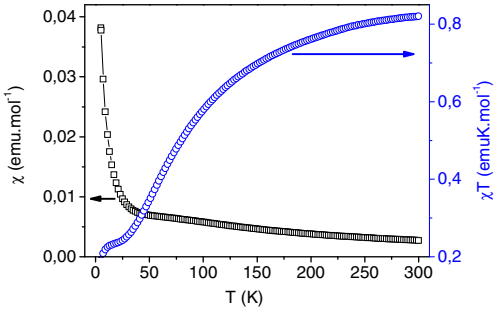

Fig. 6. Temperature variation of the magnetic susceptibilities of **1** as χ and χT vs. T plots.

reductions were observed. In the Zn(II) complex of the above ligand, formulated as Zn_2LCl_3, with chloro and phenoxo bridges connecting the Zn(II) ions, two irreversible ligand centered reductions were observed at −0.9 and −1.5 V versus Ag/AgCl reference electrode [2]. This justifies our assignment of a quasi-reversible reduction at −0.55 V to a metal centered rather than a ligand centered reduction process. It may be noted that in the related hydroxo bridged complex the Cu(II)/Cu(I) reductions could not be detected, and an irreversible reductive wave at −0.75 V in cyclic voltammetry was assigned to Cu(I)/Cu(0) process by comparison with thirteen similar complexes [2]. This was probably due to the sluggish rate of heterogeneous electron transfer for the Cu (II)/Cu(I) reduction, which broadens the reductive wave so much to render it undetectable. The Cu(II)/Cu(I) reduction could be detected for the same compound ($E^{0'}$ = 0.235 V {150 mV}) in MeCN solution with Pt electrode. Thus the Cu(II)/Cu(I) reduction potentials in such complexes are critically dependent on solvent, nature of the electrode and also on the nature of the anion present as a bridging ligand. It was previously argued that in presence of coordinated anions like azide and thiocyanate the rate of heterogeneous electron transfer increases due to the ability of such anions to adsorb on the electrode surface and thus they act as a conduit for electron transfer between the electrode and the complex [29]. This is probably the reason for nearly reversible nature of the redox couples for the present complex. On the positive side of the potential window a quasi-reversible couple at 0.75 V (132 mV) is probably due to oxidation of the phenolato oxygen to phenoxyl radical [30], while an oxidative wave at 1.28 V may be due to further ligand oxidation or oxidation of azide to azidyl radical [30].

On addition of 3,5-DTBC in 1:2 (complex: 3,5-DTBC) molar ratio, the couple at 0.06 V disappears, and two new cathodic waves at −0.15 and −0.3 V, with corresponding anodic waves at 0.15 and −0.15 V, respectively, appear (Fig. 5), which we tentatively assign to successive one electron reduction of 3,5-DTBQ to coordinated semiquinone anion radical and catecholate dianion, respectively.

3.5. Magnetic properties of complex *1*

The magnetic properties of complex **1**, in the form of χ_M and $\chi_M T$ (χ_M is the susceptibility per dinuclear unit) versus T plots, are shown in Fig. 6 in a temperature range 5–300 K. The value of χ_M at 300 K is 0.0027 $cm^3\ mol^{-1}$ and increase slightly to 30 K and then increases sharply to 0.0382 $cm^3\ mol^{-1}$ at 5 K. The $\chi_M T$ values at 300 K, 0.8203 emu K mol^{-1} (μ_{eff} = 2.56 μ_B) for **1**, which is characteristic for two non-coupled copper(II) ions with an average g factor of 2.09 ($\chi_M T = N\mu_B^2 g^2/2k$). As the temperature is lowered, the $\chi_M T$ values decrease in a monotonous manner. The curves are typical for antiferromagnetically coupled systems. The magnetic data at the very low temperatures may be influenced by the combined effect of the zero-field splitting of the triplet ground state and the intermolecular interactions between the dimeric units of **1**, as that reported in the literature [31]. The magnetic properties of **1** are comparable for similar binuclear Cu(II) complexes [32–34,11,35] (Table 4). There are two magnetic pathways: one end on azido bridge and one phenoxo bridge for complex **1** (Fig. 7). The phenoxo bridged species exhibit antiferromagnetic interaction when the angle is larger than 97.5° and the antiferromagnetic character increases with increasing angle [36]. Therefore, the expected coupling in complex **1** through

Table 4
Structural and magnetic data for **1** and a series of related compounds.

Complex	Cu–Cu (Å)	Cu–O–Cu (°)	Cu–N–Cu (°)	J (cm^{-1})	Ref.
$[Cu_2(L^1)_2(H_2O)_2(NO_3)(N_3)](NO_3)$	3.054	101.3(5)	100.5(6)	−46.77	This work
$[Cu_2(L^1)(N_3)]\cdot 2H_2O$[a]	3.100	102.06(12)	102.94(16)	−59.5	[34a]
$[Cu_2(HL)(\mu\text{-}N_3)(H_2O)(C_2H_5OH)(ClO_4)]$[b]	2.968	99.2(3)	99.9(4)	−66.2	[34b]
$[Cu_2(Famp)(1,1\text{-}N3)]\cdot(ClO_4)_2$[c]	2.993	100.5(3)	99.7(3)	−80.5	[34c]
$Cu_2L1(N_3)_2\cdot 2H_2O$[d]	3.032	101.30(12)	98.26(18)	−94.3	[34d]
$[Cu_2L(\mu_{1,1}\text{-}N_3)(N_3)_2]$[e]	3.140	101.40(5)	105.65(7)	−186.3	[34e]
$Cu_2(L)(N_3)(NO_3)_2$[f]	3.131	106.0	100.7	−194	[11]
$[Cu_2L^3(N_3)]\cdot(ClO_4)_2$[g]	3.007	100.4(3)	102.8(4)	−204	[34f]

[a] H_3L^1: 2,6-bis[{[(2-hydroxybenzyl)(*N*,*N*-(dimethylamino)ethyl)]amino}methyl]-4-methylphenol.
[b] HL: 2,6-diformyl-4-methylphenol di(benzoylhydrazone).
[c] Famp: 2,6-bis(*N*-(2-pyridylmethyl)formimidoyl)-4-methylphenolate.
[d] H_2L^1: 1,2-diaminoethane and 4-methyl-2,6-diformylphenol.
[e] HL: 2,6-diformyl-4-ethylphenol and 3-dimethylaminopropylamine.
[f] HL: 2,6-bis[4-(2-benzimidazolyl)-2-thiabutyl]-4-methylpheno.
[g] HL^3 = 4-methyl-2,6-bis[*N*-(2-pyridylethyl)formimidoyl]phenolate.

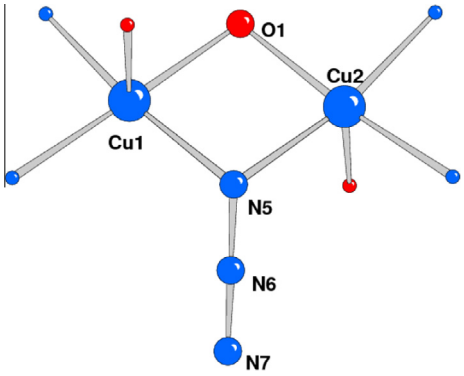

Fig. 7. Local coordination environments of Cu(II) atoms and the magnetic exchange coupling pathway for complex **1**.

the phenoxo bridge (Cu–O–Cu = 101.3°) should be antiferromagnetic. On the other hand for the azide bridges, the ferromagnetic character decreases with an increase in the Cu–N–Cu angle from 85° and shows antiferromagnetic behavior for Cu–N–Cu angle $\geqslant$104° [37]. In complex **1**, the Cu–N–Cu angle (100.5°) is less than 104°, indicating that the expected magnetic coupling would be ferromagnetic through the bridging azido group [38]. The magnetic behavior of both the phenoxo and end-on azide system depends on the orbital counter complementary effect [39]. The magnetic behavior of **1** clearly indicates that the phenoxo route dominates over the azide route. However, in the present case, the $\mu_{1,1}$-N_3 group shows a small or negligible orbital counter complementary effect, which results in antiferromagnetic coupling.

4. Conclusions

The optimum Cu–Cu separation of *ca.* 3 Å as is observed in the native enzyme (in met state) has been maintained in making the complex by employing the phenol based "end-off" compartmental ligand, 2,6-bis(*N*-ethylpyrrolidine-iminomethyl)-4-methyl-phenolato. X-ray single crystal structure analysis confirms a dinuclear copper species where two copper atoms are bridged by phenoxido and $\mu_{1,1}$-azido bridges and geometry of each copper center is distorted square pyramidal. The complex exhibits excellent catecholase activity by oxidizing not only 3,5-DTBC but also TCC, a substrate very hard to oxidize in acetonitrile as well as in DMSO medium. Electrochemical analysis reveals that the complex shows three quasi-reversible reductive couples which are tentatively assigned as Cu^{II}_2 to $Cu^{II}Cu^{I}$ and $Cu^{I}Cu^{I}$ reduction followed by reduction of $Cu^{I}Cu^{I}$ complex to $Cu^{0}Cu^{0}$ species. Variable temperature magnetic measurement has been performed and data analysis reveals that the two copper(II) ions are antiferromagnetically coupled where antiferromagnetic contribution of phenoxido bridge supersedes the ferromagnetic interaction of azido bridge.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2015.07.038.

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