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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A R T I C L E   I N F O

A B S T R A C T

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_2^{II} to $Cu^{II}Cu^I$ and Cu^ICu^I reduction followed by reduction of Cu^ICu^I complex to Cu^0Cu^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.

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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 $[Cu_2L_2(H_2O)_2(\mu_{1,1}-N_3)](NO_3)_2$ (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$_2$O)$_2$(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$_3$)$_2$·3H$_2$O (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$_2$N$_9$O$_9$: 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}; ν(H$_2$O) 3434 cm^{-1}; ν(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$_2$N$_9$O$_9$	$F(000)$	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$_2$L(H$_2$O)$_2$(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(4)	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)