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Magnetic and catalytic properties of a new copper(II)–Schiff base 2D coordination polymer formed by connected helical chains

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ABSTRACT

A dicyanamide bridged 2D polynuclear complex of copper(II) having molecular formula $[Cu_2(L) (\mu_{1,5}-dca)_2]_n$ (1) has been synthesized using the Schiff base ligand *N*,*N*'-bis(salicylidene)-1,3-diaminopentane, (**H**₂**L**) and sodium dicyanamide (dca). The complex presents a 2D hexagonal structure formed by 1,5-dca singly bridged helical chains connected through double 1,5-dca bridges. The chelating characteristics of the **H**₂**L** Schiff base ligand results in the formation of copper(II) dimer with a double phenoxo bridge presenting a very strong antiferromagnetic coupling in the copper(II) derivative (1) (*J* = -510 cm⁻¹). The dimeric asymmetric unit of 1 is very similar to the active site of the catechol oxidase and, as expected, also presents catalytic activity for the oxidation of 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butylquinone in presence of O₂, as demonstrated by kinetic studies of this oxidation reaction monitored by absorption spectroscopy resulting in high turnover number ($K_{cat} = 259 h^{-1}$).

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1. Introduction

The design and synthesis of transition metal coordination polymers are drawing the attention of coordination chemists not only because of their interesting structural features as observed in the metal-organic frameworks or porous coordination polymers but also for their many possible applications in catalysis [1], magnetism [2], light emission and electron transport processes [3]. One of the possible building blocks that can be used to construct these materials are the salen type Schiff base ligands. In this context, we [4-6] and others [7-12] have prepared a large number of metal complexes with tridentate (N₂O donor) and tetradentate (N₂O₂ donor) Schiff base ligands. These studies have shown the role played by the different transition metal ions and the Schiff base ligands in the formation of complexes with different nuclearities, topologies and dimensionalities. Thus, N₂O₂ donor Schiff bases as N,N'-bis(salicylidene)-1,3-diaminopropane, N,N'-bis(salicylidene)-1,3-diaminopentane and N,N'-bis(2-hydroxyacetophenone)propylenediimine have shown a remarkable tendency to form trinuclear phenoxo bridged complexes in presence of bridging anions or coligands [4,13-16]. Pseudohalide coligands, such as cyanide, azide, thiocyanate, and dicyanamide (dca), have been utilized to bridge transition metal–Schiff base complexes in order to explore and modify the magnetic properties and the network topology as well as to increase the dimensionality of the resulting coordination polymers [17–19]. The flexibility in the coordination modes shown by the dicyanamide anion (dca) [20] has been extensively used to create many different molecular architectures [21–25] with interesting magnetic properties ranging from weak antiferromagnetic to strong ferromagnetic couplings and even long range magnetic ordering [26–28]. Among the several coordination modes of dca, the $\mu_{1,5}$ -bridging mode is by far the most usual one with ca. 450 known structures out of the ca. 650 known compounds containing dca either as ligand or as counter ion. In fact this coordination mode has already been observed in various complexes with NNO donor Schiff base by us and other research groups [29–33].

Besides their magnetic properties, copper(II) complexes are also extensively studied for their bio-catalytic activity since copper plays a very important role in many biological systems. Thus, it is usually found in metalloenzymes involved in processes like hydroxylation, oxygen transport, electron transfer, and catalytic oxidation [34–36]. Among these copper enzymes, catecholoxidases are ubiquitous plant enzymes belonging to the oxido-reductase class, with a dinuclear copper(II) center at the active site. This catalyzes the two-electron oxidation of a broad range of *o*-diphenols (catechols) to the corresponding quinones, coupled with the reduction of molecular oxygen to water (Scheme 1) [37,38]. This reaction

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Scheme 1. Oxidation of the 3,5-di-tert-butylcatechol by the catalyst.

is of great importance in medical diagnosis for the determination of the hormonally active catecholamines such as adrenaline, noradrenaline and dopamine [39]. Quinones thus produced are very much reactive to autopolymerize resulting in melanin, a brown pigment, responsible to protect tissues against pathogens and insects.

In the isolated catecholoxidases, the copper was found to be EPR-silent and was assigned to an antiferromagnetically spin-coupled copper(II)-copper(II) pair [40]. XAS investigations on the native met forms of catecholoxidases from Lycopus europaeus and Ipomoea batatas have revealed that the active site consists of a dinuclear copper(II) core [41], 2.9 Å apart and are bridged by a hydroxide ion. Each metal is further coordinated by three histidine residues. Although the active site composition of different forms of catechol oxidases are established from X-ray crystallography, its catalytic mechanism is not fully understood yet. Krebs and his group proposed a monodentate asymmetric coordination of the substrate to the dicopper core of the enzyme where as a bidentate bridging substrate coordination was predicted by Solomon and his group [34–36]. After that Mukherjee and Mukherjee reported that copper(II) complexes are reduced to copper(I) during catalysis and electron transfer from catechol to the copper(II) complex occurs via the formation of a copper-catechol intermediate [38]. For the present work the coordination environment of the copper(II) complex $[Cu_2(L)(\mu_{1.5}-dca)_2]_n$ (1) resembles that of the catecholoxidase as the asymmetric unit contains strongly antiferromagnetically coupled dicopper metal core coordinated by N/O donor ligand. Moreover the penta coordinated copper(II) centers are able to provide vacant coordination sites for the binding of 3,5-di-tert-butylcatechol (3,5-DTBC) in a bridging mode. Hence this structural similarity prompted us to investigate whether **1** can act as a model system mimicking the activity of catecholoxidase.

In the context of these two potential applications, here we report the synthesis, X-ray crystal structure and physicochemical properties of a new polymeric copper(II) complex formed with a N₂O₂ donor Schiff base ligand and dicyanamide (dca) as coligand, formulated as $[Cu_2(L)(\mu_{1,5}-dca)_2]_n$ (1). Thus, the copper(II) derivative (1) represents a 2D coordination polymer formed by chiral helical chains connected through double dca bridges to form a hexagonal layer with very strong antiferromagnetic interactions and catecholoxidase-like activity.

2. Experimental

2.1. Materials

All solvents were of reagent grade and used without further purification. 1,3-Diaminopentane and salicylaldehyde were purchased from Aldrich Chemical Company. Sodium dicyanamide was bought from Fluka. Copper nitrate trihydrate was purchased from E. Merck, India and was used as received. The chemicals 3,5-DTBC (3,5-di-*tert*-butylcatechol), MES (2-(*N*-morpholino) ethanesulfonicacid), Hepes (2-[4-(2-hydroxyethyl)piperazin-1yl]ethanesulfonicacid) and Tris (2-amino-2-hydroxymethyl-propane-1,3-diol) used in catalytic activity studies were purchased from Acros Organics.

2.2. Syntheses

2.2.1. Synthesis of the Schiff base ligand (H_2L)

The Schiff base ligand, $OHC_6H_4CH=NCH_2CH_2CH(CH_2CH_3)N=CHC_6H_4OH$ [*N*,*N*'-bis(salicylidene)-1,3-diaminopentane (**H**₂**L**)] was prepared using a published procedure (Scheme 2) [15]. Anal. Calc. for C₁₉H₂₂N₂O₂: C, 73.55; H, 7.09; N, 9.03. Found: C, 73.58; H, 7.11; N, 9.04%.

2.2.2. Synthesis of the complex $[Cu_2(L)(\mu_{1.5}-dca)_2]_n$ (1)

In order to synthesize **1** Cu(NO₃)₂·3H₂O (0.362 g, 1.5 mmol) was dissolved in 20 mL of warm methanol. About 10 mL of methanolic solution (yellow) of the Schiff base (**H**₂**L**) (0.354 g, 1 mmol), was added to it drop wise with stirring. An aqueous solution of sodium dicyanamide, Na(dca) (0.133 g, 1.5 mmol) was added drop wise into the stirring solution. After dca addition was completed the mixture was allowed to stir for 5 min with gentle warming to avoid precipitation of the complex. The dark green solution was filtered and kept at room temperature for crystallization by slow evaporation for overnight to yield brown prismatic crystals suitable for X-ray crystallography. Crystals were isolated by filtration and airdried. Yield: 0.2715 g (75%). Anal. Calc. for $C_{23}H_{20}Cu_2N_8O_2$: C, 48.63; H, 3.52; N, 19.73. Found: C, 48.70; H, 3.59; N, 19.82%.

2.3. Physical measurements

The Fourier transform infrared spectra were recorded in the range 4000-400 cm⁻¹ on a Perkin-Elmer RX I FT-IR spectrophotometer with solid KBr pellets. The electronic spectra were recorded at 300 K on a Perkin-Elmer Lambda 40 (UV-Vis) spectrometer by diffuse reflectance technique using paraffin oil matrix in a 1 cm quartz cuvette in the range 200-800 nm. Electrochemical measurements were performed at 20 °C on a VersaStat-Potentio-Stat II cyclic voltammeter using HPLC grade DMF as solvent where tetrabutylammonium perchlorate was used as supporting electrolyte. Platinum and saturated calomel electrodes (SCE) were the working and the reference electrodes in the process, respectively. C. H and N microanalyses were carried out with a Perkin-Elmer 2400 II elemental analyzer. The magnetic susceptibility measurements were carried out in the temperature range 2-300 K with an applied magnetic field of 0.1 T on a polycrystalline sample of 1 (mass = 43.76 mg) with a Quantum Design MPMS-XL-5 SQUID susceptometer. The isothermal magnetization was performed on the same sample at 2 K with magnetic fields up to 5 T. The susceptibility data were corrected for the sample holder previously measured using the same conditions and for the diamagnetic contributions of the salt as deduced by using Pascal's constant tables (χ_{dia} = -312.8 emu mol⁻¹). The spectrophotometric measurements for the catalytic studies were carried out with a Perkin-Elmer Lambda 20 UV-Vis spectrophotometer. Mass spectra of 1 was analyzed in a Qtof Micro YA263 mass spectrometer.

2.4. X-ray crystallography

The X-ray diffraction study for **1** was carried out at 110(2) K on a brown prismatic single crystal ($0.42 \times 0.18 \times 0.15 \text{ mm}^3$). The intensity data of **1** were collected with 'Xcalibur, Ruby, Gemini' diffractometer device using ω scan technique with Cu K α radiation ($\lambda = 1.54184$ Å). The structure was solved by direct methods using the shellxs-97 program and refined by full-matrix leastsquares methods in shellxl-97 program [42]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares based on F^2 . The H atoms were generated geometrically and were included in the refinement in the riding model approximation. The lattice constants were refined by least-square refinement using 10 463 total reflections ($4.44 < \theta < 74.02^\circ$), 4618 unique reflection



N2O2 donor set with phenoxo bridging character

Scheme 2. Synthesis of the Schiff base H₂L and its coordination mode.

 $(R_{int} = 0.0244)$. Structure solution and refinement based on 4618 observed reflections with $I > 2\sigma(I)$ and 337 parameters gave final R = 0.0609, wR = 0.1557 with goodness-of-fit 1.101. Selected crystallographic data, experimental conditions and relevant features of the structural refinements for the complex are summarized in Table 1.

2.5. Methodology for catecholase-like activity of 1

The catalytic oxidation of the model substrate 3,5-di-*tert*-butylcatechol (3,5-DTBC) by **1** was evaluated spectrophotometrically in dioxygen-saturated DMF along with blank experiments in presence of dioxygen. A pH-dependence study was carried out to determine the pH value at which catecholase activity is maximum. For this pH dependence studies, catalyst aqueous solutions were prepared with MES (pH 5.5, 6.0 and 6.5), Hepes (pH 7.0, 7.5, 8.0 and 8.5) and Tris (pH 9.0) and standardized NaOH or HNO₃ were mixed with equal volumes of 3,5-DTBC solution in DMF. In all cases, a rapid increase in the reaction rate is observed above pH \approx 7.5. To reduce the influence of the deprotonation of 3,5-DTBC at high pH, the catalytic activity experiments were performed at pH 8.0 and to remove the effect of pH on the spontaneous reaction the same solution was used without adding the complex as an internal reference.

The catalytic oxidation rate of 3,5-DTBC (3,5-di-*tert*-butylcatechol) by **1** was monitored spectrophotometrically recording the increase in absorbance at 395 nm, corresponding to the formation of the quinone product 3,5-DTBQ (3,5-di-*tert*-butyl-*o*-benzoquinone). The initial reaction rates were determined from the slope of the trace at 395 nm during the first 30 min of the reactions, when the absorption at 395 nm increases linearly. To determine the dependence of the rates on the substrate concentration and various kinetic parameters, 5.75×10^{-5} M solution of **1** was treated with 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 equivalent of 3,5-DTBC in DMF under aerobic condition. A kinetic treatment on the basis of the Michaelis–Menten approach was applied and the results were evaluated from Lineweaver–Burk double reciprocal plots. To reduce the statistical error, every measurement was carried out at least thrice.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy

The IR spectrum of **1** was analyzed and compared with that of the free ligand H_2L in the region 4000–400 cm⁻¹. A strong sharp absorption band around 1631 cm⁻¹ in the spectrum of the Schiff base ligand can be assigned to the C=N stretching. Upon complexation with the metal, this band is shifted to 1618 cm^{-1} in **1** as a result of the coordination of the imine nitrogen to the metal center [43-45]. The ligand showed a well defined band at 3537 cm⁻¹ due to O-H stretching which disappeared in the complex, indicating the deprotonation of the Schiff base ligand upon complexation. The strong phenolic C–O absorption band at 1214 cm⁻¹ observed in the spectrum of the protonated free ligand, H_2L , is shifted to lower frequencies (1156 cm^{-1} in **1**), supporting the deprotonation and the coordination of the phenolic oxygen atoms to the metal centers, as confirmed by the structure of the complex [45]. Complex 1 showed sharp absorption bands in the region 2160-2380 cm⁻¹ which indicate the presence of the dicyanamide ligand. The dicyanamide anion in NaN(CN)₂ showed three sharp and strong characteristic bands in the frequency region 2290-2170 cm⁻¹ which are attributed to $v_{as} + v_s$ (C=N) combination modes (2286 cm⁻¹), v_{as} (C \equiv N) (2232 cm⁻¹) and v_s (C \equiv N) (2179 cm^{-1}) [20]. Upon complexation these bands shift towards higher frequencies along with further splitting. In 1 the doubly splitted $v_{as} + v_s$ (C=N) bands were located at 2371 (m, with shoulder on the high frequency side) and 2306 (s) cm⁻¹. The v_{as} (C \equiv N) band appeared at 2240 (s) cm⁻¹ and the bifurcated v_s (C \equiv N) bands were detected at 2172 (s) and 2169 (s) cm⁻¹ (s, strong; m, medium). The splitting and displacement of the bands towards higher

Table 1	
Crystal data for	$[Cu_2(L)(\mu_{1.5}-dca)_2]_n$ (1).

Formula	$C_{23}H_{20}Cu_2N_8O_2$
Formula weight	567.55
Т (К)	110(2)
λ (Å)	1.54184
Crystal system	monoclinic
Space group	P2(1)/c
Unit cell dimensions	
a (Å)	9.7603(3)
b (Å)	12.0653(3)
<i>c</i> (Å)	19.9097(6)
α (°)	90
β (°)	91.720(3)
γ (°)	90
$V(Å^3)$	2343.53(12)
Ζ	4
D_{calc} (mg/m ³)	1.609
Absorption coefficient (mm ⁻¹)	2.562
F(000)	1152
Crystal size (mm ³)	$0.42\times0.18\times0.15$
θ (°)	4.44-74.02
Index ranges	$-12\leqslant h\leqslant 12$, $-11\leqslant k\leqslant 14$,
	$-24 \leqslant l \leqslant 20$
Reflections collected	10 463
Independent reflections	$4618 [R_{int} = 0.0244]$
Completeness to θ = 74.02°	97.2%
Absorption correction	semi-empirical
Maximum and minimum transmission	1.00000 and 0.71030
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	4618/9/337
Goodness-of-fit (GOF) on F^2	1 101
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0609 \ wR_2 = 0.1557$
R indices (all data)	$R_1 = 0.0677 \ wR_2 = 0.1597$
Largest difference peak and hole	0.827 and -0.658
$(e Å^{-3})$	5.52, and 0.050
(011)	

frequencies clearly show the bidentate bridging mode of dca ligand [46] in **1** as is evidenced by the X-ray crystal structure. The ligand coordination to the metal center is substantiated by a band appearing at 450 cm⁻¹ in **1** which is mainly attributed to ν_{Cu-N} in the complex.

3.2. UV-Vis spectroscopy

UV–Vis spectrum of the complex was recorded at 300 K with the diffuse reflectance technique in paraffin oil matrix. Three distinct CT bands appeared in the spectrum of **1** at 209, 263 and 345 nm. The high energy band at 209 nm in **1** can be considered as an aromatic $\pi - \pi^*$ intraligand CT transition [47]. The band at 263 nm can be attributed to the $n-\pi^*$ transition within the ligand [48]. The L \rightarrow M charge transfer transition band appeared around 345 nm [47]. For a square pyramidal copper(II) environment the one electron orbital sequence is $d_{xz} = d_{yz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$ and generally a broad visible band appears in the range 550–660 nm. In contrast for a TBP complex the d–d band usually appears at $\lambda > 800$ nm [49–51]. A broad d–d transition band of much weaker intensity was found in the spectrum of **1** at 670 nm supporting that the copper(II) centers have square-pyramidal geometry.

3.3. Cyclic voltammetry

The electrochemical behavior of **1** was studied in DMF medium at platinum electrode with tetrabutylammonium perchlorate as supporting electrolyte at 10, 20, 50 and 100 mV s⁻¹ scan rates. The electrochemical data are summarized in Table 2 and the cyclic voltammograms at 10 and 50 mV s⁻¹ scan rates are shown in Fig. 1. It is seen in the literature [52–54] that binuclear Cu^{II} complexes with endogenous diphenoxo bridges undergo electrochemical

 Table 2

 Cyclic voltammetry data for the red-ox process of 1 at platinum electrode.

Scan rate	$E_{\rm pc}$	$E_{\rm pa}$	$\Delta E_{\rm p}$	$E_{1/2}^{\circ}$
$(mV s^{-1})$	V (vs. SCE)	V (vs. SCE)	V	V
Step 1				
10	-0.468	-0.026	0.442	-0.247
20	-0.569	-0.00875	0.560	-0.289
50	-0.651	-0.00875	0.642	-0.329
100	-0.728	-0.009	0.719	-0.368
Step 2				
10	-1.123	-1.052	0.071	-1.087
20	-1.164	-1.035	0.129	-1.099
50	-1.141	-	-	-
100	-1.029	-	-	-

 $\begin{array}{l} \Delta E_p = E_{pa} - E_{pc}, E_{1/2}^{*} = (E_{pa} + E_{pc})/2, \Delta E_{1/2}^{\circ} = E_{1/2}^{\circ} \; (\text{step 1}) - E_{1/2}^{\circ} \; (\text{step 2}). \\ K_{com} = [\text{Cu}^{II}\text{Cu}^{I]}^{2} / [\text{Cu}^{II}\text{Cu}^{II}] [\text{Cu}^{IC}u^{I}] = \exp[nF(\Delta E_{1/2}^{\circ})/RT] = 2.84 \times 10^{14} \; (\text{for scan rate 10 mV s}^{-1}) \; \text{and } 8.66 \times 10^{13} \; (\text{for scan rate 20 mV s}^{-1}). \end{array}$

reductions via two one electron charge transfer steps with a separation of ca. 0.35–0.80 V.

Step 1 :
$$Cu^{II}Cu^{II} \stackrel{+e}{\underset{-e}{\leftarrow}} Cu^{II}Cu^{I}$$

Step 2 : $Cu^{II}Cu^{I} \stackrel{+e}{\underset{-e}{\leftarrow}} Cu^{I}Cu^{I}$

It is also seen that the second step is electrochemically reversible at slow scan rates but not at high scan rates whereas the first step has a greater probability of being electrochemically reversible than the second step [52]. It is examined for phenoxo bridged binuclear macrocyclic complexes [55] that the first couple (Cu^{II}Cu^{II}) shows near Nernstian behavior while the second couple (Cu^{II}Cu^{II}) undergoes adsorption at the electrode. For the present complex (1) containing a bis($\mu_{1,1}$ -phenoxo)bridged dinuclear Cu^{II} core, during the cathodic scan two well separated reduction peaks (A and B in Fig. 1) corresponding to the steps 1 and 2 were observed at all scan rates (Table 2). During the reverse scan two quasi reversible oxidation peaks were observed at 10 and 20 mV s⁻¹ scan rates (B' and A' in Fig. 1) which correspond to the reverse processes of steps 2 and 1, respec-



Fig. 1. Cyclic voltammogram of **1** in DMF at a platinum electrode at 20 °C, black: at 10 mV s⁻¹ scan rate, red: at 50 mV s⁻¹ scan rate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tively. At higher scan rates (50 and 100 mV s⁻¹) no oxidation peak was observed for the reverse process of step 2. ΔE_p increases at higher scan rates (Table 2), showing the quasi reversible nature of the electron transfer processes. All these behaviors are in accordance with the redox properties of similar kind of doubly phenoxo bridged dinuclear Cu^{II} complexes reported previously [52,55].

The stability of the mixed valent species (Cu^{II}Cu^{II} species) in the equilibrium mixture is rationalized by the comproportionation constant (K_{com}), which is 2.84×10^{14} for 10 mV s^{-1} and is 8.66×10^{13} for 20 mV s⁻¹ scan rates (Table 2). The K_{com} values are in good agreement with those reported for doubly phenoxo bridged dinuclear copper complexes [56,57] and signify considerable interaction between the two phenoxo bridged copper centers in **1** [58].

3.4. ESI mass spectrum of 1

Positive ion electrospray mass spectrum of 1 in dilute acetonitrile solution give two intense signals at m/z 372 and m/z 765 (Fig. 2). The former signal corresponds to the species [LCu]⁺ and the latter can be attributed to a combined species $[{Cu_2(L)(\mu_{1.5}$ $dca_{2}Cu(dca_{2})^{+}$. The structural assignments for such ions are also supported by their characteristic isotopic distributions particularly affected by the presence of copper (63Cu:65Cu of 1:0.44). It is possible that a portion of the molecular ion $[Cu_2(L)(\mu_{1.5}-dca)_2]^+$ undergoes fragmentation in two components [LCu and Cu(dca)₂]. The Cu (dca)₂ component being associated with the molecular ion $[Cu_2(L)(\mu_{1,5}-dca)_2]^+$ appear as a signal at m/z 765. It is not very certain that whether this fragmentation occurs due to dissociation mechanism in acetonitrile solution or during the ionization process within the mass spectrometer. If the molecular fragmentation of 1 occurs in the gas phase during the ionization process [59] then it is possible that the solid state structure of **1** retains in solution also. On the other hand it is also reported that ESI-MS is a very gentle technique to transfer preformed ions from solution to the gas phase [60]. Hence there is another possibility that the fragmentation occurs during solvation in acetonitrile and a mono metallic species [LCu] and a trimetallic species $[{Cu_2(L)(\mu_{1,5}-dca)_2}Cu]$ (dca)₂] exist in equilibrium. Then it is evident that at least the phenoxo bridged dinuclear core of the asymmetric unit retains in solution.

3.5. Crystal structure of $[Cu_2(L)(\mu_{1,5}-dca)_2]_n$ (1)

The ORTEP diagram of the asymmetric unit of the complex $[Cu_2(L)(\mu_{1,5}-dca)_2]_n$ (1) is shown in Fig. 3 and the bond distances



Fig. 2. Positive ion ESI mass spectrum of 1 in acetonitrile solution.



Fig. 3. ORTEP view of the asymmetric unit of **1**. Displacement ellipsoids drawn at the 40% probability level. Suffix A symmetry code: -x, y + 1/2, -z + 1/2; suffix B symmetry code: -x, -y + 1, -z.

and bond angles around the metal centers are listed in Tables 3 and 4, respectively. The asymmetric unit of **1** contains two dipositive Cu ions, a Schiff base ligand connecting both metal ions through a double phenoxo bridge and two independent dca anions that connect each copper(II) dimer with its three closest neighbors.

All dca ligands are bridging in the $\mu_{1,5}$ mode and generate a 2D structure formed by interconnected dimers with two types of inter-dimer connections: a single dca bridge (centered at N5) connecting each dimer with two neighboring copper(II) dimers along the *y*-direction and a double one (centered at N2) connecting each dimer with its closest copper(II) dimer along the *z*-direction (Fig. 4).

The dimeric asymmetric unit can be formulated as $[Cu_2(L)(\mu_{1,5}-dca)_2]$ and it comprises a dimetallic core consisted of two five coordinate metal centers linked by the phenoxo oxygen atoms of the Schiff base. The metal centers (Cu1 and Cu2) enclosed by the Schiff base are closest to square pyramidal geometry as defined by the Addison parameter, $\tau = 0.13$ and 0.14 for Cu1 and Cu2, respectively, $[\tau = |\beta - \alpha|/60^\circ$ where β and α are the two largest angles around the central atom; $\tau = 0$ and 1 for perfect square pyramidal and trigonal bipyramidal geometries, respectively] [61]. In **1** the Cu1 is chelated by the deprotonated Schiff base ligand (L^{2-}) through its two phenoxo oxygen atoms (O1 and O21) and two imino nitrogen atoms (N9 and N13) (Fig. 5). The axial position of this Cu1 ion is occupied by

Table 3Selected bond distances (Å) for 1.

Cu1-021	1.948(3)
Cu1-N9	1.953(5)
Cu1-01	1.965(3)
Cu1-N13	1.986(6)
Cu1-N3#1	2.347(4)
Cu1–Cu2	2.9737(9)
Cu2-N1	1.958(4)
Cu2-N4	1.980(4)
Cu2-N6#2	2.154(4)
Cu2-01	1.994(3)
Cu2-021	1.998(3)

Table 4
Selected bond angles (°) for 1

ciccica bolia aligies () for 1.			
021-Cu1-N9	167.77(19)		
021-Cu1-O1	75.45(13)		
N9-Cu1-O1	92.76(19)		
021-Cu1-N13	91.0(2)		
N9-Cu1-N13	99.5(2)		
01-Cu1-N13	160.1(2)		
O21-Cu1-N3#1	89.20(15)		
N9-Cu1-N3#1	94.32(17)		
01-Cu1-N3#1	90.79(15)		
N13-Cu1-N3#1	103.82(18)		
N1-Cu2-N4	94.82(16)		
N1-Cu2-O1	158.07(15)		
N4-Cu2-O1	89.56(15)		
N1-Cu2-O21	92.45(15)		
N4-Cu2-O21	149.84(15)		
01-Cu2-021	73.71(14)		
N1-Cu2-N6#2	100.10(16)		
N4-Cu2-N6#2	102.60(17)		
01-Cu2-N6#2	99.89(14)		
O21-Cu2-N6#2	104.85(15)		

Symmetry transformations used to generate equivalent atoms in **1**: #1 - x, -y + 1, -z; #2 - x, y + 1/2, -z + 1/2; #3 - x, y - 1/2, -z + 1/2.

the N3 atom of dca bridge connecting the Cu1 ion with the Cu2 ion of a neighboring dimer. In the structure of **1** Cu1 is 0.17 Å off the square plane defined by O1, N9, N13 and O21. The square plane around Cu2 is formed by two bridging phenoxo oxygens (O1 and O21) from the deprotonated Schiff base ligand (L^{2-}) and two nitrogen ends (N1 and N4) of two $\mu_{1,5}$ -bridging dca anion and another dicyanamide nitrogen end (N6) occupies the apical position. The Cu2-axial dca N bond is elongated due to Jahn–Teller distortion [2.154(4) Å]. Cu2 is 0.406 Å off the mean square plane passing through O1, N4, N1 and O21 displaced towards N6.

The four intradimer Cu–O bond distances are in the range 1.948–1.998 Å in **1** and the two Cu–O–Cu bond angles are very similar (97.36° and 97.78°) in **1** with a dihedral angle in the central Cu₂O₂ unit of ca. 29.6°. The Cu—Cu separation is 2.9737(9) Å in **1**.

Here the bridging character of dca is worth mentioning. The N3 atom of a μ_{15} -bridging dca which occupies the axial position of Cu1 ion connects that Cu1 ion with the Cu2 ion of a neighboring dimer (A). The N4-containing dca bridge connects the Cu2 with another Cu2 atom of the neighboring dimer B (Fig. 6). Finally, the N6 containing dca bridge connects Cu2 with a Cu2 atom of a third neighboring $[Cu_2(L)(\mu_{1.5}-dca)_2]$ dimer (C). Thus each dimer is connected to its three neighboring dimers (A, B and C) through a double dca bridge (with dimer A) and through two single dca bridges (with dimers B and C) in form of six membered metallacyclic rings (counting each dimetallic core as one node). These six membered rings extend in two dimensions giving rise to an undulating sheet in the 100 plane shown in Fig. 4. Between the undulating sheets the benzene rings in the Schiff base interdigitate but in 1 the centroid to centroid distance exceeds 3.9 Å which is too long for $\pi - \pi$ interactions. The connectivity of the single dca bridges from Cu2 to symmetry equivalent centers can be viewed as a helical chain running parallel to the y axis. As expected from the achiral space group, there is an equal number of right and left handed helical chain (Fig. 7).

3.6. Magnetic properties of 1

The thermal variation of the molar magnetic susceptibility per copper(II) dimer times the temperature ($\chi_m T$) for **1** shows at room temperature a value of ca. 0.16 emu K mol⁻¹ (Fig. 8). This value is much lower than the expected one (ca. 0.75 emu K mol⁻¹) for two isolated copper(II) *S* = 1/2 ions. When cooling down the sam-



Fig. 4. View of the 2D structure of **1** showing the interconnected dimers. Only the dca units and the coordination sphere of the copper(II) ions are shown for clarity.



Fig. 5. Coordination sphere of the two Cu ions in the copper(II) dimer of 1 showing the main bond distances (in Å) and angles (in °).

ple, the $\chi_m T$ product linearly decreases down to ca. 150 K to reach a value of ca. 0.015 emu K mol⁻¹ (Fig. 8). Below 150 K the $\chi_m T$ product remains almost constant down to ca. 50 K and below this temperature it shows an additional decrease to reach a value of ca. 0.005 emu K mol⁻¹ which remains almost constant down to 2 K. This behavior indicates that **1** presents a strong antiferromagnetic coupling, which is already operative at room temperature, responsible for the linear decrease observed in the $\gamma_m T$ product from room temperature down to ca. 150 K. The residual value observed in the temperature range 150-50 K can be attributed to the presence of a small amount of "monomeric" impurities, as is customary in many polymeric copper(II) complexes. This "monomeric" impurity is further coupled through a weaker antiferromagnetic interaction, responsible for the additional decrease observed below 50 K. This behavior is clearly confirmed by the thermal variation of χ_m that shows a broad rounded maximum at ca. 300 K, corresponding to a strong antiferromagnetic coupling and a second maximum at ca. 40 K that corresponds to a weaker antiferromagnetic coupling between the monomeric impurities (inset in Fig. 8). At low temperatures χ_m shows a divergence corresponding to the presence of a small amount of paramagnetic isolated impurities.

According to the crystal structure, **1** consists of copper(II) dimers where the copper(II) ions are connected through double phenoxo bridges connecting two equatorial positions of the square



Fig. 6. Perspective view of **1** showing a complete Cu dimer and the four Cu atoms that are connected to it. Color code: N = blue, C = brown, O = pink, Cu = green. Only the major component of the disordered ethyl group is shown and H atoms are omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. View of the two helical chains with different chirality in **1**. Only the Cu1 and the single dca bridges are shown for clarity.

pyramidal copper(II) ions. These copper(II) dimers are further connected through dicyanamide (dca) bridges to three neighbor dimers to construct a hexagonal-2D undulating sheet-like polymer (Fig. 4). This structure leads to a quite complex 2D exchange pathway with at least three different exchange constants since one of the three interdimer connections is made through two equivalent equatorial-axial dca bridges (centered at N2) whereas the other two interdimer connections are made through equivalent single equatorial-axial dca bridges (centered at N5). Fortunately, to a first approximation, we can consider that the intradimer double phenoxo bridges connecting two equatorial positions give rise to a much stronger (antiferromagnetic) coupling since they present a strong overlap with the magnetic (x^2-y^2) orbitals on both copper(II) ions. Assuming that this coupling is by far the most important one, we can neglect the dca bridges and fit the magnetic properties to the simple Bleaney–Bowers model for an S = 1/2 dimer plus a monomeric S = 1/2 contribution [62,63]. This model satisfactorily reproduces the magnetic properties of 1 above 50 K with g = 1.854(9), J = -734(6) K = -510(4) cm⁻¹ and a paramagnetic impurity of 2.1% (solid line in Fig. 8). Note that although at low temperatures the small amount of paramagnetic impurities pres-



Fig. 8. Thermal variation of the $\chi_m T$ product per copper(II) dimer for **1**. Inset shows the thermal variation of χ_m . Solid line is the best fit to the S = 1 dimer model.

ent an antiferromagnetic coupling, this extra contribution is very difficult to simulate since it corresponds to a very small monomeric fraction and the coupling constant is also much smaller than the intradimer one. Although it is possible to fit the magnetic properties in the whole temperature range (with quite similar parameters, except the paramagnetic impurity that decreases from 2.1% to ca. 0.7%), the weak antiferromagnetic coupling appearing as a maximum at ca. 40 K is not well reproduced (dashed line in Fig. 8). The low *g* value found can be attributed to the very low signal of the sample at high temperatures, as a consequence of the very high antiferromagnetic coupling. This low signal precludes an accurate determination of the true contribution of the sample since the diamagnetic contributions are very similar to the paramagnetic one at high temperatures.

The isothermal magnetization at 2 K shows a very small saturation value at 5 T (ca. 0.014 μ_B , coming from the small amount of paramagnetic impurity), confirming the strong antiferromagnetic coupling in this compound.

As already described, 1 can be considered as a copper(II) dimer with a double equatorial-equatorial phenoxo bridge (Fig. 5). This kind of bridge is well known to provide strong antiferromagnetic coupling since the magnetic orbitals (x^2-y^2) present a good overlap with the orbitals of the oxygen atoms. In fact, magneto-structural correlations for copper(II) complexes with double phenoxo bridges indicate that the magnetic exchange linearly depends on the Cu-O-Cu bond angle and on the Cu-Cu distance. The larger the Cu-O-Cu bond angle, the stronger the antiferromagnetic coupling, with a crossing point at ca. 95.7° [64–66]. In **1** if we apply these magneto-structural correlations to the two Cu-O-Cu bridging angles (ca. 97.8° and 97.4°) we expect a coupling constant of ca. -450 cm^{-1} , in agreement with the experimental value found in this compound (-510 cm^{-1}) . Regarding the Cu–Cu distance, the application of the magneto structural correlations to the Cu--Cu distance in **1** (2.9736(8)Å) leads to an expected coupling of ca. -400 cm^{-1} , also in quite good agreement with the experimental value.

3.7. Catecholase-like activity of 1

Among the different catechols used in catecholoxidase model studies, 3,5-di-*tert*-butylcatechol (3,5-DTBC) is the most widely used substrate due to its low redox potential for the quinone –catechol couple, which facilitates its oxidation to the corresponding quinone 3,5-di-*tert*-butylquinone (3,5-DTBQ), and to the presence of bulky substituents, that slow down further oxidation

reactions such as ring opening. The detection of the oxidation of 3,5-DTBC to the corresponding 3,5-DTBQ can be easily followed by the development of the absorption band at about 400 nm [67,68].

Catalytic studies were performed at 25 °C in N,N-dimethylformamide solution owing to the good solubility of the complex as well as substrate. Blank experiments showed that in absence of catalyst the transformation of 3,5-DTBC to 3,5-DTBQ does not take place. Evaluating the catalytic property of 1, we note that it exhibits considerable catecholase activity in presence of dioxygen. Therefore, initially, a pH-dependence study was carried out to determine the pH value at which catecholase activity is at a maximum. Although in all cases, catecholase activity was observed, **1** exhibits almost no catalytic activity below pH 7.5 with a fast increase of the reaction rate above this pH value (Fig. 9). Hence, the catalytic activity experiments were performed at pH 8.0. The pH dependence of the catechol oxidation reaction is due to the fact that at alkaline pH the water molecules present in the medium (present in solvent or in buffer or generated by the reduction of O₂ during the catalytic cycle) form hydroxide ions which help in deprotonation of the 3,5-DTBC substrate. Thus the catecholate anions coordinate to the Cu(II)–Cu(II) moiety of complex 1 either by coordinating at the sixth coordination sites of the two Cu(II) ions or by replacing the dca ligands [69,70]. In order to minimize the effect of pH on the spontaneous reaction, the same solution was used without adding the complex as an internal reference.

The kinetic studies on the oxidation of 3,5-DTBC were carried out by the method of initial rates by monitoring the increase in the characteristic quinone (3,5-DTBQ) absorption band at 395 nm as a function of time (Fig. 10). A linear relationship for the initial rates and complex concentration is observed, meaning a first-order dependence on the catalyst concentration for the system. At low concentrations of 3,5-DTBC a first-order dependence of the substrate concentration could be observed. Also saturation kinetics was found at high substrate concentrations. In order to determine the kinetic parameters, the Michaelis-Menten approach which was originally developed for enzyme kinetics, was applied. The results were evaluated from Lineweaver-Burk double reciprocal plots from which the parameters such as maximum velocity $(V_{\rm MAX}$ = 1.8 × 10⁻⁷ M s⁻¹), Michaelis binding constant ($K_{\rm M}$ = 7.8 × 10^{-4} M) and the turnover number (K_{cat} = 259 h⁻¹) which is actually the dissociation constant for the complex-substrate intermediate were obtained for 1. The turnover number for catechol oxidase is $8254.8 \times 10^3 \text{ h}^{-1}$. Though **1** showed much less turnover number compared to catechol oxidase the value is quite comparable to the dinuclear copper(II) complexes reported in the literature [38,70,71].



Fig. 9. Dependence of the reaction rates on pH for the oxidation of 3,5-DTBC catalyzed by **1**. The reactions were performed in DMF/aqueous buffer saturated with O_2 [MES (pH 5.5, 6.0 and 6.5), Hepes (pH 7.0, 7.5, 8.0 and 8.5) and Tris (pH 9.0)], [complex] = 5.75×10^{-5} M and [3,5-DTBC] = 2.87×10^{-3} M at $25 \,^{\circ}$ C.

Some of the crucial factors dictating the catecholase activity can now be highlighted based on many investigations correlating various structural parameters of the dicopper(II) complexes with their activity; viz., the distance between the copper(II) centers [72,73], the nature of the bridging group between the copper ions [38,69,74], electronic properties of the complexes [34–41,75,76] and the geometric change of the dicopper core [77]. Furthermore, the factors such as the number of donor sites, nature of the donors, and the rigidity of the ligand or the bridging moiety imposing strain in the complex have also been found to play a vital role [67].

Dinuclear copper complexes are generally more reactive towards the oxidation of catechols than are the corresponding mononuclear-species [78] and these complexes catalyze oxidation if the Cu…Cu distance is <5 Å [79]. The synthesized complex **1** showed high catalytic activity regarding the oxidation of 3,5-di-tert-butylcatechol to 3,5-di-tert-butylquinone as evident from the observed hyperchromism of the absorption band at 395 nm recorded every 30 min time interval during the course of the reaction (Fig. 10). As observed in the structure of **1**, the metallic site of the dinuclear asymmetric unit is easily accessible and the short phenoxo bridged intra dimer Cu1-Cu2 distance (2.9736(8) Å) will allow a bridging catechol coordination compatible with the distance between the two o-diphenol oxygen atoms (a Cu–Cu distance of 3.25 Å was measured for the unique o-catecholate-bridged dicopper complex described in the literature) [80]. It is emphasized that this distance is 2.9 Å in the enzyme, which is also a μ -hydroxo dicopper complex. Similar conclusions had been reached by Krebs [67].



Fig. 10. Increase of the quinone band at 395 nm after addition of 3,5-DTBC (2.87×10^{-3} M) to a solution of 1 (5.75×10^{-5} M) in DMF at 25 °C. The spectra were recorded every 30 min. Inset shows the variation of absorbance with time (min).

In this paper, we have described the synthesis of a new dicyanamide bridged 2D polymeric complex of copper with a N₂O₂ donor Schiff base ligand and its applications in magnetic and catalytic fields. The antiferromagnetically coupled dicopper metal core with Cu-Cu distance 2.974 Å resembles the active site of the plant enzyme catechol oxidase and show good catecholase activity. Thus a relevant structure-function correlation has been established among the structure of **1** and its magnetic and catalytic properties. Though most of the activities of the complex are due to the metal and the Schiff base ligand fragment the dicyanamide linker also plays some crucial role to form a 2D undulating sheet like metal organic framework. Furthermore, the presence of vacant coordination sites on the square planar chelated Cu1 atom and specially on the non-chelated Cu2 ion offers up to 1 + 3 bridging points (if we assume penta-coordination for the copper(II) ions). The addition of a highly potentially bridging ligand as dca has led, as expected, to the formation of up to four dca bridges connecting the vacant positions of the copper ions. This coordination mode generates a 2D coordination polymer with helical -Cu-dca-Cu- chains that are further connected through double dca bridges to form a 2D layer with a hexagonal topology.

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Appendix A. Supplementary material

CCDC 754866 contains the supplementary crystallographic data for 1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.06.024.

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