



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

Dipali Sadhukhan^a, Aurkie Ray^a, Ray J. Butcher^b, Carlos J. Gómez García^c, Bülent Dede^d, Samiran Mitra^{a,*}

^a Department of Chemistry, Jadavpur University, Raja S.C. Mullick Road, Kolkata 700032, West Bengal, India

^b Department of Chemistry, Howard University, 2400 Sixth Street, NW Washington, DC 20059, USA

^c Instituto de Ciencia Molecular ICMol, Universidad de Valencia, Parque Científico, 46980 Paterna, Spain

^d Faculty of Sciences and Arts, Chemistry Department, Süleyman Demirel University, 32260 Isparta, Turkey

ARTICLE INFO

Article history:

Received 10 February 2011

Received in revised form 2 June 2011

Accepted 10 June 2011

Available online 16 June 2011

Keywords:

2D coordination polymer

Helical chains

Copper(II)–Schiff base complex

Antiferromagnetic interaction

Catecholase activity

ABSTRACT

A dicyanamide bridged 2D polynuclear complex of copper(II) having molecular formula $[\text{Cu}_2(\text{L})(\mu_{1,5}\text{-dca})_2]_n$ (**1**) has been synthesized using the Schiff base ligand *N,N'*-bis(salicylidene)-1,3-diaminopentane, (**H₂L**) 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 **H₂L** 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**) ($J = -510 \text{ cm}^{-1}$). 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 O_2 , as demonstrated by kinetic studies of this oxidation reaction monitored by absorption spectroscopy resulting in high turnover number ($K_{\text{cat}} = 259 \text{ h}^{-1}$).

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

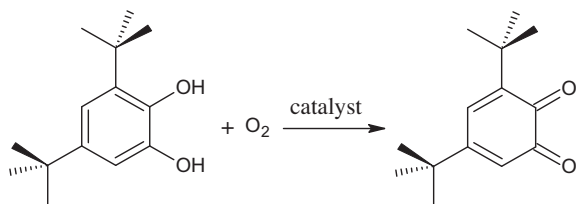
The design and synthesis of transition metal coordination polymers are drawing the attention of coordination chemists not only because of their interesting structural features as observed in the metal-organic frameworks or porous coordination polymers but also for their many possible applications in 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 (N_2O donor) and tetradentate (N_2O_2 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, N_2O_2 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

* Corresponding author. Tel.: +91 33 2414 2779; fax: +91 33 2414 6414.

E-mail address: smitra_2002@yahoo.com (S. Mitra).



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 *Lycopodium 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 $[\text{Cu}_2(\text{L})(\mu_{1,5}\text{-dca})_2]_n$ (**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 N_2O_2 donor Schiff base ligand and dicyanamide (dca) as coligand, formulated as $[\text{Cu}_2(\text{L})(\mu_{1,5}\text{-dca})_2]_n$ (**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)ethanesulfonic acid), Hepes (2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid) and Tris (2-amino-2-hydroxymethylpropane-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, $\text{OHC}_6\text{H}_4\text{CH}=\text{NCH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{N}=\text{CHC}_6\text{H}_4\text{OH}$ [*N,N'*-bis(salicylidene)-1,3-diaminopentane (H_2L)] was prepared using a published procedure (Scheme 2) [15]. Anal. Calc. for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$: 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 $[\text{Cu}_2(\text{L})(\mu_{1,5}\text{-dca})_2]_n$ (**1**)

In order to synthesize **1** $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (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_2L) (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 air-dried. Yield: 0.2715 g (75%). Anal. Calc. for $\text{C}_{23}\text{H}_{20}\text{Cu}_2\text{N}_8\text{O}_2$: 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 $4000\text{--}400\text{ cm}^{-1}$ 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-Potentiostat 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 ($\chi_{\text{dia}} = -312.8\text{ emu mol}^{-1}$). 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 $K\alpha$ radiation ($\lambda = 1.54184\text{ \AA}$). The structure was solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares methods in SHELXL-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

Download English Version:

<https://daneshyari.com/en/article/10571121>

Download Persian Version:

<https://daneshyari.com/article/10571121>

[Daneshyari.com](https://daneshyari.com)