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Ligand centered radical pathway in catechol oxidase activity with a trinuclear zinc-based model: Synthesis, structural characterization and luminescence properties

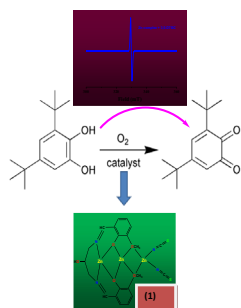
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HIGHLIGHTS

- Synthesis and characterization of a zinc(II)–Schiff base complex.
- Both ligand and complex show good fluorescence properties in solution.
- The zinc complex mimics catecholase significantly.
- Ligand centered radical mechanistically catalyzes the reaction.

GRAPHICAL ABSTRACT

A trinuclear zinc(II)–Schiff base complex has been employed to mimic catechol oxidase activity. This zinc–Schiff base complex exhibits significant catechol oxidation in methanol through ligand centered pathway, which is the rare example among the redox innocent zinc complexes till date.



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ABSTRACT

A new trinuclear zinc(II) complex, $[\text{Zn}_3(\text{L})(\text{NCS})_2](\text{NO}_3)_2 \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**1**), of a (N,O)-donor compartmental Schiff base ligand ($\text{H}_2\text{L} = \text{N,N}'\text{-bis}(3\text{-methoxysalicylidene})\text{-1,3-diamino-2-propanol}$), has been synthesized in crystalline phase. The zinc(II) complex has been characterized by elemental analysis, IR spectroscopy, UV–Vis spectroscopy, powder X-ray diffraction study (PXRD), ^1H NMR, EI mass spectrometry and thermogravimetric analysis. PXRD revealed that **1** crystallizes in $P-1$ space group with $a = 9.218 \text{ \AA}$, $b = 10.849 \text{ \AA}$, $c = 18.339 \text{ \AA}$, with unit cell volume is $2179.713 (\text{\AA})^3$. Fluorescence spectra in methanolic solution reflect that intensity of emission for **1** is much higher compared to H_2L and both the compounds exhibit good fluorescence properties. The complex **1** exhibits significant catalytic activities of biological relevance, viz. catechol oxidase. In methanol, it efficiently catalyzes the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) to corresponding quinone via formation of a dinuclear species as $[\text{Zn}_2(\text{L})(3,5\text{-DTBC})]$. Electron Paramagnetic Resonance (EPR) experiment suggests generation of radicals in the presence of 3,5-DTBC and it may be proposed that the radical pathway is probably responsible for conversion of 3,5-DTBC to 3,5-DTBQ promoted by complex of redox-innocent Zn(II) ion.

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Introduction

Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest because of their unusual configurations, structural lability, and sensitivity to molecular environments as functional materials [1–3]. No other metal has as many functions in living organisms as the metal “zinc”. The development of synthetic analogs for the active sites of different metalloenzymes containing polynuclear metal centers has become an attractive approach for obtaining information concerning the mechanisms involved in their catalytic cycles [4–6]. It is no surprise that di- and trinuclear Zn^{II} complexes have attracted particular interest as synthetic structural mimics of the active site of a range of metalloenzymes, such as zinc-dependent aminopeptidases, metallo-β-lactamases, and alkaline phosphatases [7–9]. Zinc(II) Schiff base complexes have often been found to be photochemically active [10]. Substrates, in principle, can bind to zinc by the substitution of coordinated solvent molecules or by association, thus increasing the coordination number. This behavior is typical of Lewis acids, and thus zinc can act like protons in the task. Many features of zinc, such as its ability in assisting Lewis acid activation, nucleophile generation, fast ligand exchange, and leaving group stabilization, make Zn^{II} ideal for the catalysis of hydrolytic reactions [11,12].

In the active sites of numerous metalloenzymes, two adjacent metal centers act cooperatively in the transformation of substrate molecules. This is particularly true for biological oxidase or oxygenase activity involving molecular oxygen (O₂), in which the metal ions serve to activate the kinetically inert O₂ and the combined redox power of the two metal ions is used to mediate and to control the multielectron redox reactions. In view of the great importance of oxidation reactions in industrial and synthetic processes and of the ongoing search for new and efficient oxidation catalysts, it is of paramount interest to elucidate the basic functional principles that govern such bimetallic reactivity of natural enzymes [13].

Compartmental Schiff base ligands that contain different pockets can assemble different 3d–3d and/or 3d–4f systems which lead to coordination compounds with important magnetic properties. This feature is also employed for modeling active sites in biological systems [14]. This compartmental Schiff-base ligand, N,N'-bis(3-methoxysalicylidene)-1,3-diamino-2-propanol has been employed to the isolation of magnetically interesting compounds [15]. With the aim to develop polynuclear Zn^{II} complex having potential to mimic the active sites of different metalloenzymes, we have synthesized, characterized and explored the bio-catalytic activity of a trinuclear Zn–Schiff base complex.

Experimental

Preparation of the ligand and complex

Chemicals, solvents and starting materials

High purity *O*-vanilin (Sigma, Germany), 2-hydroxy-1,3-diaminopropane (Aldrich, USA), zinc(II) nitrate hexahydrate (Merck, India), ammonium thiocyanate (Merck, India) and all other solvents were purchased from the respective concerns and used as received. 3,5-*di*-*tert*-butylcatechol (3,5-DTBC) was obtained from Sigma Aldrich Corporation (St. Louis, MO, USA). All other chemicals and solvents were of analytical grade and were used as received without further purification.

Preparation of H₂L and zinc complex (1)

The Schiff base ligand, H₂L was prepared prepared according to literature method [15]. To prepare the Schiff base ligand, 2-hydroxy-1,3-diaminopropane (0.0890 g, 1 mmol) was refluxed

with *O*-vanilin (0.3046 g, 2 mmol) in 20 ml dehydrated alcohol for 6 h and after 7–10 days yellowish orange colored compound was isolated from solution, which was dried and stored *in vacuo* over CaCl₂ for subsequent use. Yield: 3.420 g (87%). Anal. Calc. for C₁₉H₂₂N₂O₅ (H₂L): IR (KBr, cm⁻¹): 3365 (ν_{OH}), 1618 (ν_{C=N}), 1333, 1245 (ν_{phO}); UV-Vis (λ_{max}, nm): 255, 315, 403; ¹H NMR (δ ppm, 400 Mz, DMSO-*d*₆) δ = 13.55 (s, 2H), 9.92 (s, 2H), 7.26–6.90 (Ar-H, 6H), 5.94 (s, 1H), 3.93 (s, 6H) ppm. EI-MS (*m/z*) 359.16 [H₂L+H⁺]⁺ (see Scheme 1).

A methanolic solution (5 ml) of H₂L (0.358 g, 1 mmol) was added dropwise to a solution of Zn(NO₃)₂·6H₂O (0.596 g, 2 mmol) in the same solvent (10 ml). After that, ammonium thiocyanate (0.152 g, 2 mmol) in methanol was added to the reaction solution. The yellow solution was kept in air for slow evaporation to obtain crystalline product.

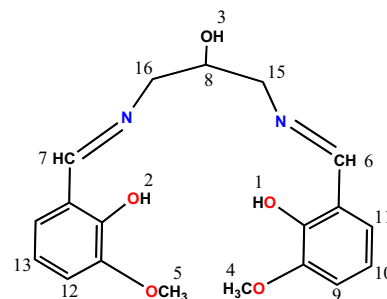
Yield: 0.672 g (70% based on metal salt). Anal. Calc. for C₂₂H₂₆N₆O₁₃S₂Zn₃ (1): C, 31.35; H, 3.11; N, 9.97. Found: C, 31.39; H, 3.26; N, 9.99. IR (KBr, cm⁻¹): 3408, 3155 (ν_{OH(free)}), 2090 (ν_{NCS}), 1639, 1616 (ν_{C=N}), 1386 (ν_{NO₃}); UV-Vis (λ_{max}, nm): 232, 269, 353; ¹H NMR (δ ppm, 500 Mz, DMSO-*d*₆) δ = 8.392, 8.384 (d, 2H), 7.24–6.70 (Ar-H, 6H), 5.24 (s, 1H), 3.84–3.78 (–OCH₃, 6H), ppm; EI-MS (*m/z*) 843.72 [1+H⁺]⁺.

Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. Fourier Transform Infrared (FT IR) spectra (KBr discs, 4000–300 cm⁻¹) were recorded using a FTIR-8400S SHIMADZU spectrophotometer in the range 400–3600 cm⁻¹. Ground-state absorption and steady-state fluorescence measurements were made with a Jasco model V-530 UV-Vis spectrophotometer and Hitachi model F-4010 spectrofluorimeter, respectively. The ¹H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX-500 MHz spectrometer. The Electron Paramagnetic Resonance (EPR) spectrum was recorded on a Bruker EMX-X band spectrometer. The crystalline phase was identified by powder X-ray diffraction patterns (PXRD) of the materials by using a BRUKER AXS (Model: 8D-ADVANCE) diffractometer with a Cu K_α radiation source under continuous scanning mode in the range 8–60°. Electrospray ionization (EI) mass spectrum was recorded using a Q-tof-micro quadrupole mass spectrometer. Thermal analysis was carried out on a PerkinElmer Diamond TG/DTA system up to 900 °C in a static nitrogen atmosphere with a heating rate of 10 °C/min.

Catalytic oxidation of 3,5-DTBC

In order to examine the catecholase activity of the complex, a 10⁻⁴ M solution of **1** in methanol solvent was treated with 100 equiv. of 3,5-*di*-*tert*-butylcatechol (3,5-DTBC) under aerobic conditions at room temperature. Absorbance vs. wavelength



Scheme 1. Structure of the ligand.

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