



Catecholase Activity of a Mononuclear Cobalt(III) Azido Complex

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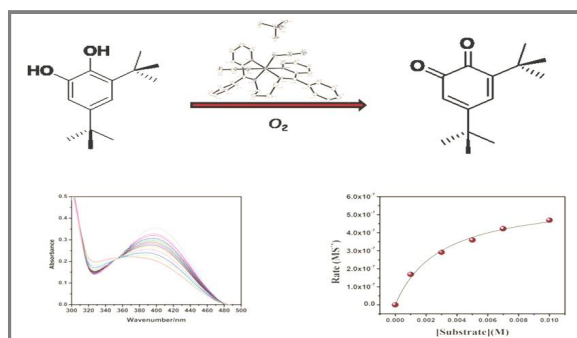
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ABSTRACT

One mononuclear cobalt(III) azido complex of the type $[Co(L)(N_3)_2]ClO_4$ (**1**) [$L = N,N'$ -(bis(pyridine-2-yl)benzylidene)-1,4-butanediamine] behaves as an effective catalyst towards the oxidation of 3,5-di-tert-butylcatechol in dichloromethane (DCM) to its corresponding quinone derivative in aerial oxygen. The reaction follows Michaelis-Menten enzymatic reaction kinetics with a turnover number (K_{cat}) of $4.68 h^{-1}$.

Graphical Abstract



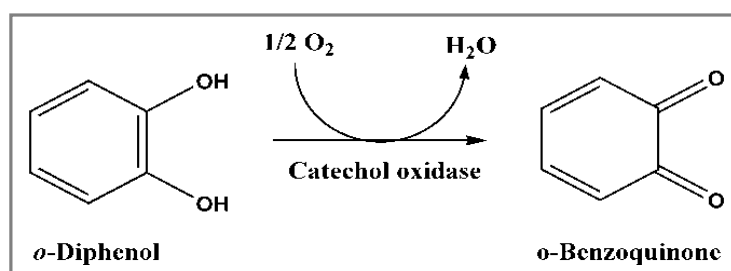
Catecholase activity

Keywords: Cobalt complex, Schiff base, Catecholase activity, Michaelis-Menten kinetics.

INTRODUCTION

Oxidation of a range of *o*-diphenols (catechols) in presence of the enzyme catecholase to corresponding quinone (Scheme 1) is known as catecholase activity [1-3] which is a very important process as a defence mechanism against invasion of pathogens in plants. Crystal structure determination of the met-form of catecholase in 1988 [4] revealed that the active site of the enzyme consists of a hydroxo bridged dicopper(II) centre in which each copper(II) centre is coordinated to three histidine nitrogens and adopts a trigonal pyramidal environment with one nitrogen in the apical site. Just after the publication of active site structure of the enzyme catecholase, a good number of researchers round the globe started to synthesize different dinuclear Cu(II) compounds to mimic the enzyme activity [1-3]. Not only dinuclear Cu(II), but also some mononuclear Cu(II) complexes [5]

and complexes of some transition metals other than Cu(II) like manganese [6], nickel [7], iron [8], cobalt [9], zinc [10], vanadium [11], etc also appeared in literature. We are also actively working in this field during last few years in designing different non-copper complexes which are showing catecholase activity [12, 13]. Herein, a report of the catecholase activity of a mononuclear cobalt(III) azido complex of the type $[\text{Co}(\text{L})(\text{N}_3)_2]\text{ClO}_4$ (**1**) [$\text{L}=\text{N},\text{N}'$ -(bis(pyridine-2-yl)benzylidene)-1,4-butanediamine] is presented which has been structurally characterized earlier (Figure 1) [14]. **1** behaves as an effective catalyst towards the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) in aerial oxygen.



Scheme 1. Catecholase activity.

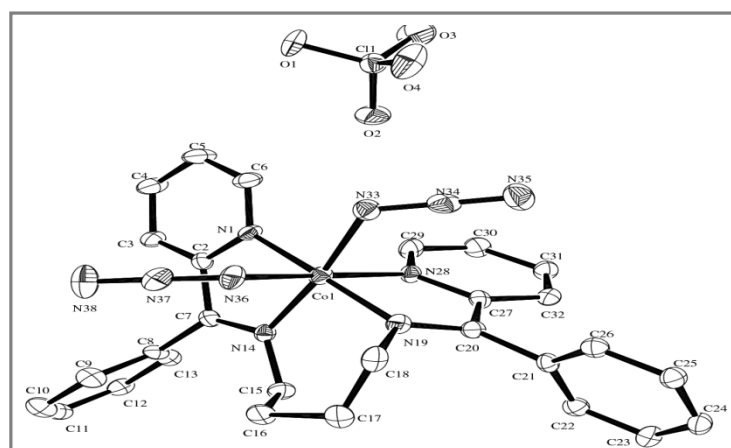


Figure 1. ORTEP of $[\text{Co}(\text{L})(\text{N}_3)_2]\text{ClO}_4$ (**1**).

MATERIALS AND METHODS

High purity 2-benzoylpyridine (Lancaster, UK), butane-1,4-diamine (Lancaster, UK), sodium azide (E. Merck, India), cobalt(II) perchlorate hexahydrate (Sigma Aldrich, India), 3,5-di-*tert*-butylcatechol (Aldrich, UK) and all other solvents were purchased from the respective concerns and used as received. UV-Vis spectrum was recorded using a Shimadzu UV-Vis 2450 spectrophotometer.

RESULTS AND DISCUSSION

Catecholase activity of **1, spectrophotometric study:** In order to study the catecholase activity of the complex **1**, 3,5-DTBC with two bulky *t*-butyl substituents on the ring and low quinone-catechol reduction potential has been chosen as substrate. This makes it easily oxidized to the corresponding *o*-quinone, 3,5-di-*tert*-butylquinone (3,5-DTBQ) which is highly stable and shows a maximum absorption at 401 nm in DCM. Solution of **1** was treated with 100 equivalents of 3,5-DTBC under

aerobic conditions. The repetitive UV-Vis spectral scan was recorded in pure DCM (Figure 2). After addition of 3,5-DTBC, the time dependent spectral scan shows very smooth growing of quinone band at 400 nm, as reported by Krebs *et al* [15], indicates the formation of the respective quinone derivative, 3,5-DTBQ which was purified by column chromatography. The product obtained from the solvent was isolated in high yield (65%) by slow evaporation of the eluant and was identified by measuring melting point ($\sim 110^{\circ}\text{C}$) [16].

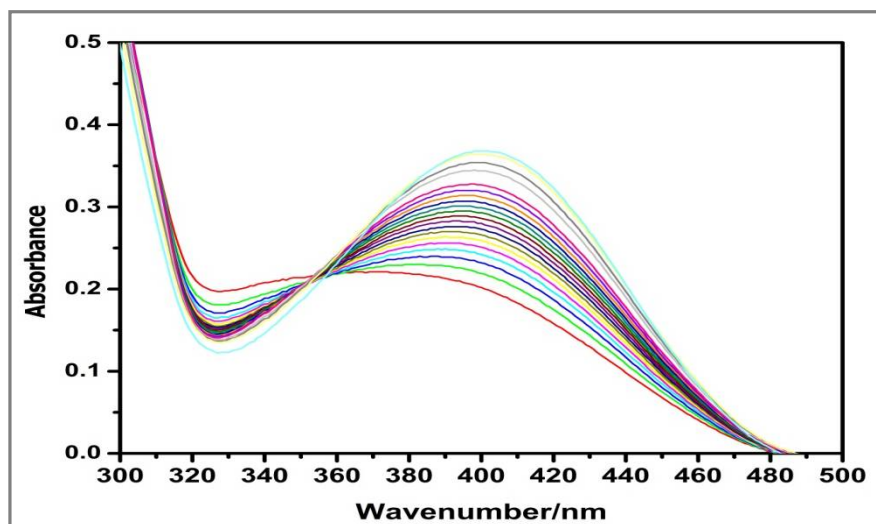


Figure 2. Change in spectral pattern of reaction of **1** with 3,5-DTBC in Dichloromethane after observing the reaction for 2 h.

To find out the comparative reaction velocity between 3,5-DTBC and **1**, the reaction kinetics between **1** and 3,5-DTBC was studied by observing the time dependent change in absorbance at a wavelength of 400 nm, which is characteristic of 3,5-DTBQ in solution. The colour of the solution gradually turns deep brown in DCM indicative of gradual conversion of 3,5-DTBC to 3,5-DTBQ. A first-order catalytic reaction is observed, with velocity (V_{\max}) 1.30×10^{-7} .

Enzyme kinetics study: Enzymatic kinetic experiments were performed UV-Vis spectrophotometrically, thermostated at 25°C with complex **1** and the substrate 3,5-DTBC in DCM. 0.05 mL of the complex solution, with a constant concentration of 1×10^{-4} M, was added to 2 ml of 3,5-DTBC of a

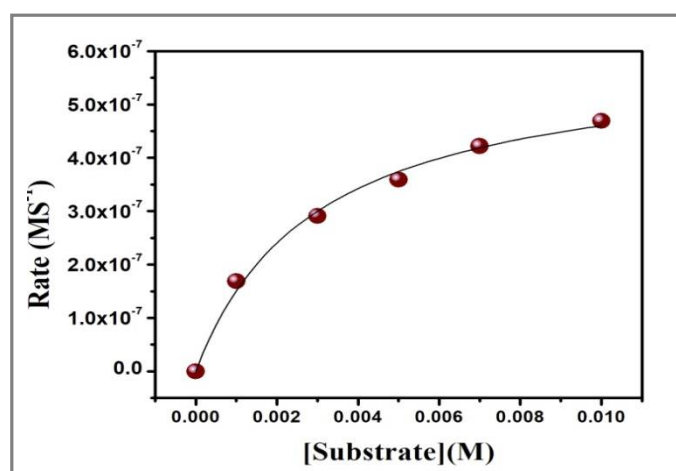


Figure 3. Plot of rate vs. [substrate] in the presence of **1** in dichloromethane.

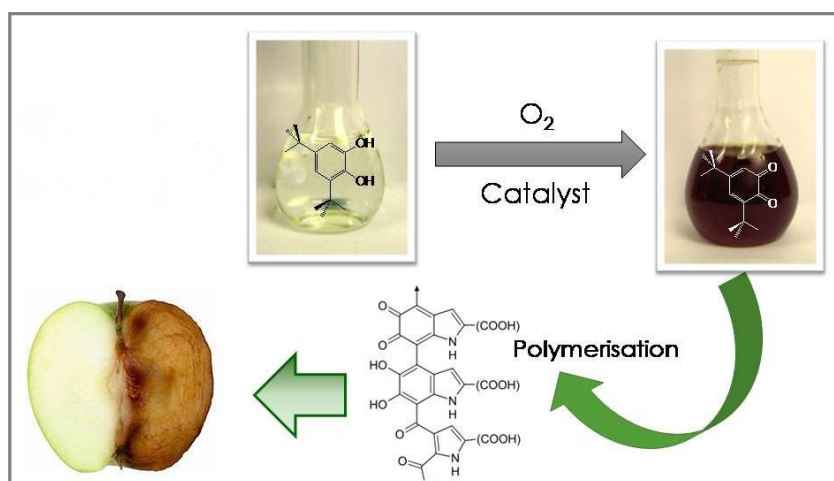
particular concentration (varying its concentration from 1×10^{-3} (M) to 1×10^{-2} (M)) to achieve the ultimate concentration of the complex as 1×10^{-4} (M). The conversion of 3,5-DTBC to 3,5-DTBQ was monitored with time at a wavelength of 400 nm for solution in DCM. The rate for each concentration of the substrate was determined by the initial rate method. The rate versus concentration of substrate data were analyzed on the basis of Michaelis-Menten approach (Figure 3) to find the values of the kinetic parameters V_{\max} , and K_{cat} . The kinetic parameters are listed in table 1. The turnover numbers (K_{cat}) are found to be 4.68 h^{-1} .

Table 1. Kinetic parameters for the oxidation of 3,5-DTBC catalyzed by 1

Compound	Solvent	V_{\max} (M s^{-1})	Std. error	K_{cat} (h^{-1})
1	DCM	1.30×10^{-7}	2.98×10^{-6}	4.68

APPLICATION

The oxidation of catechol or its derivative to quinone is a very slow process. But the participation of metal complex, which acts as the catalyst, makes it a fast process. The obtained quinone autopolymerises to form melanin which acts as a defence mechanism in cut open plants and fruits against the invasion of external pathogens (Scheme 2). These can a very promising and useful process to convert *o*-diphenols to its corresponding *o*-quinones in a considerably less amount of time. Work is going on in this direction to make good catalysts with high turnover numbers.



Scheme 2. Catecholase activity ultimately resulting in formation of melanin.

CONCLUSION

Synthesis and structural characterization of a reported Co (III) azido complex is presented in this research article. The complex is found to be catecholase active, following Michaelis-Menten kinetics in DCM solvent with appreciable turnover number (K_{cat}) and maximum velocity (V_{\max}).

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