

DISSERTATION: REVIEW REPORT



Gokhale Memorial Girls' College

1/1, Harish Mukherjee Rd, Gokhel Road, Bhowanipore, Kolkata, West Bengal
700020

Department Of Chemistry

UNDER THE GUIDANCE OF:

Dr. ANANGAMOHAN PANJA

TOPIC

**PHENOXAZINONE SYNTHASE: BIOMIMETIC
FUNCTIONAL MODELS ON IRON COMPLEXES.**

SUBMITTED BY: AMREEN SOHAIL

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ABSTRACT:

The impetus to modelling of enzyme active sites comes from their potential to provide insight to the mechanistic pathways of the native enzymes, establishing the role of that particular metal in the active site and to design better catalysts inspired by nature. Most of the metalloenzyme are capable of activating molecular oxygen due to the presence of the metal ions. Among the various metalloenzymes, phenoxazinone synthase (PHS) is an enzyme that is of interest for its oxidizing ability to generate phenoxazinone. In this review we discuss the progress made so far in the area of Fe-based models on phenoxazinone synthase enzyme. The studies on phenoxazinone synthase are quite detailed and the mechanistic pathways reasonably well disseminated as discussed here.

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ZINC BASED CATECHOL OXIDASE: BIOMIMETIC FUNCTIONAL MODEL AND MECHANISTIC PATHWAY

BSc Chemistry (Honours) Semester – VI (Under CBCS) Examination, 2022

Course: CEMA DSE – B4 (Dissertation)

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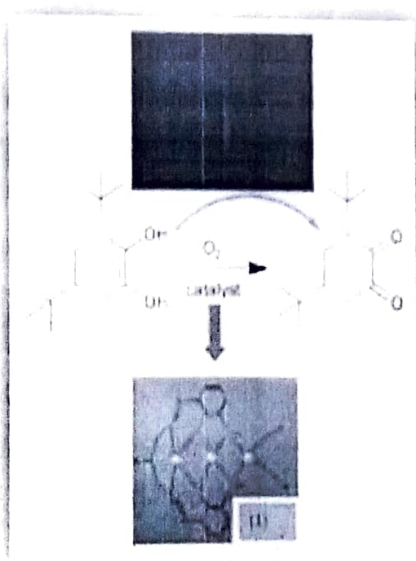
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ABSTRACT

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' -bis(3-methoxysalicylidene)-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** exhibit significant catalytic activities of biological relevance, viz. catechol oxidase. In methanol, it efficiently catalyses the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) to corresponding quinone via formation of a Di nuclear 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.

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 centred pathway, which is the rare example among the redox innocent zinc complexes till date.



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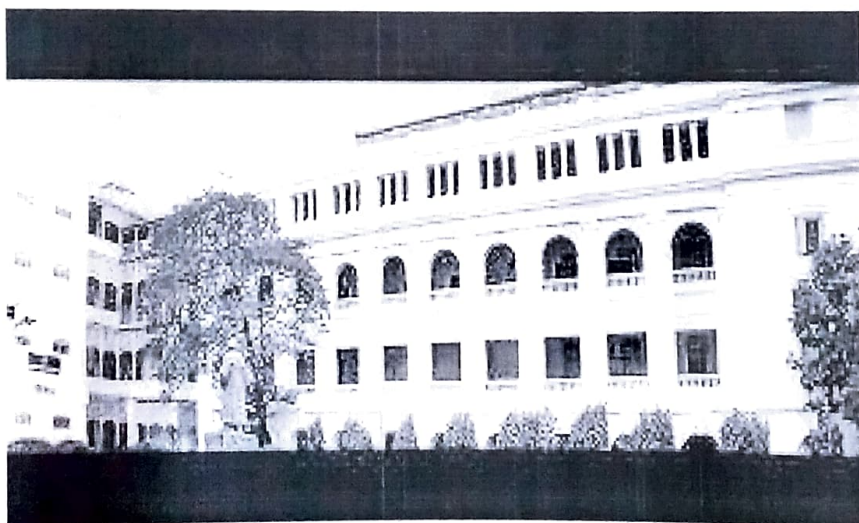
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REVIEW ARTICLES

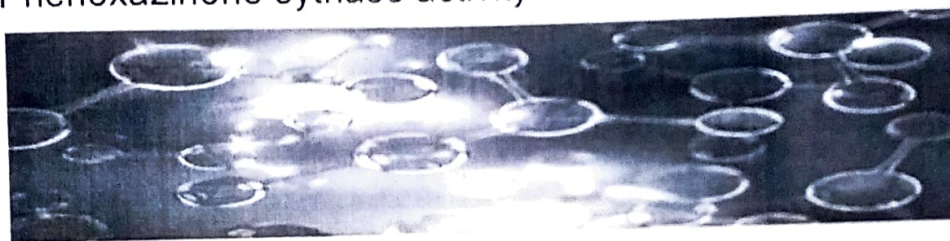
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1/1, Harish Mukherjee Rd, Gokhale Road, Bhawanipore, Kolkata, West Bengal 700020

DEPARTMENT OF CHEMISTRY

TOPIC

Phenoxazinone synthase activity of a Mn based complex



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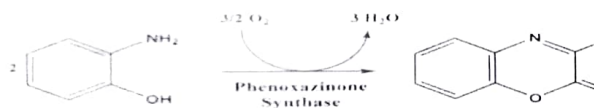
ABSTRACT:

This review describes recent progress in modeling the active sites Phenoxazinone Synthase that activate dioxygen to carry out several key reaction in nature. This review (upto 2021) is the continuation of the review done (upto 2015) by S.K. Dey and A. Mukherjee (Coord. chem. Rev. 310, (2016) 80-115). The impetus to modeling of enzyme active sites comes from their potential to provide insight to the mechanistic pathways of the native enzymes, establish the role of that particular metal in the active site and to design better catalysts inspired by nature. Most of the metallo enzymes are capable of activating molecular oxygen due to the presence of the metal ions. The name phenoxazinone synthase (PHS; 2-aminophenol Oxygen oxidoreductase) is used for the enzyme catalysing the oxidative coupling of substituted o-aminophenols to produce phenoxazines.

In this review we discuss the progress made so far in the area of phenoxazinone synthase modeling. The review shows that PHS has been widely attempted for modeling the active site. The biomimetic studies strongly suggest that among the various metal ions probed for modeling the catalytic activity of PHS, MnII/III based systems are so far the most promising candidates apart from the nature's choice of Cu(II) ion. PHS like activity suggests the potential of such mimics may extend beyond the biological modeling and provide insight to the various possible mechanistic pathways that may be adapted by a model complex.

INTRODUCTION:

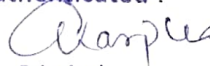
Phenoxazinone synthase. This topic is taken from bioinorganic chemistry. It is a metalloenzyme containing copper. It acts as a catalyst. Eg. it catalyzes the coupling of 2-aminophenols to form the 2-aminophenoxazinone chromophore during the synthesis of actinomycin D.



1. ACTIVATION OF MOLECULAR OXYGEN

Oxidation reaction is a fundamentally important component of organic synthesis and plays an important role in rendering the desired functionality to the intermediates of valuable compounds such as pharmaceuticals, agrochemicals, and other fine chemicals. Molecular oxygen is an ideal oxidant because of its availability directly from air rendering it inexpensive and environmentally benign. The challenges faced to activate molecular oxygen for its use in oxidation reactions is due to its kinetically inert nature. A major problem while using dioxygen in chemical transformation is that its reactivity is not easily controlled and often may lead to low selectivity and over-oxidation. Nature has evolved an elegant solution to overcome the kinetic barrier of dioxygen activation by using transition metal incorporated in proteins, the so called 'metalloenzyme'. Inorganic chemists have largely exploited the concept of nature by designing oxygen activation catalysts which act as small molecule mimics of the metalloenzymes and help to understand the mechanistic pathways. Using the knowledge of co-ordination chemistry, redox potential and electronic factors, the enzymes donor sites are modeled with small molecule called ligands, which are then incorporated with metals to form complexes that are probed as structural and functional models[1].

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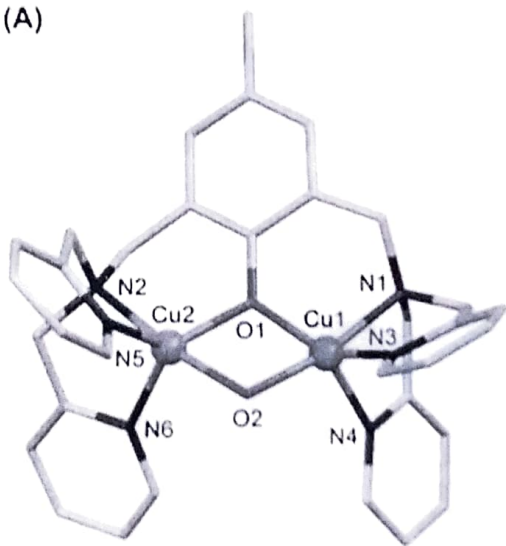
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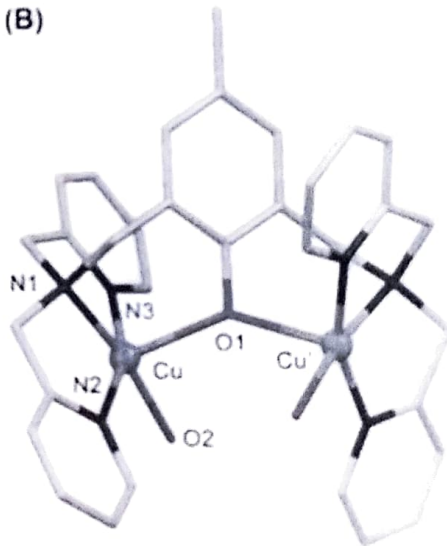
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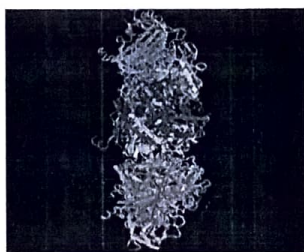
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Department of Chemistry

REVIEW ARTICLE

TOPIC: COBALT BASED PHENOXAZINONE OXIDASE: BIOMIMETIC FUNCTIONAL MODEL AND MECHANISTIC STUDIES

UNDER THE GUIDANCE OF: DR. ANANGAMOHAN PANJA



SUBMITTED BY: RAUSHNI KHATOON

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1. Abstract:

The impetus to modeling of enzyme active sites comes from their potential to provide insight to the mechanistic pathways of the native enzymes, establishing the role of that particular metal in the active site and to design better catalysts inspired by nature. Most of the metalloenzyme are capable of activating molecular oxygen due to the presence of the metal ions. Among the various metalloenzymes, phenoxazinone synthase (PHS) is an enzyme that is of interest for its oxidizing ability to generate phenoxazinone. In this review we discuss the progress made so far in the area of co-based models on phenoxazinone synthase enzyme. The studies on phenoxazinone synthase are quite detailed and the mechanistic pathways reasonably well disseminated as discussed here.

2. Introduction:

2.1 Activation of molecular oxygen

Oxidation reactions are fundamentally important component of organic synthesis and play an important role in rendering the desired functionality to the intermediates of valuable compounds such as pharmaceuticals, agrochemicals, and other fine chemicals.[1-3] For economic and environmental reasons, the oxidation processes of bulk chemical industries predominantly involve the use of molecular oxygen as the primary oxidant[4-8]. The application of oxidation reactions in scaled-up synthesis is limited due to the use of heavy metals, thermal hazards, and moderate chemoselectivity for highly functionalized compounds in most oxidation reactions[9,10]. Classical oxidation methods with stoichiometric quantities of inorganic oxidants are toxic and enrich the environmental pollution. That is why oxidations using catalytic amount of activator which can activate molecular oxygen with minimum chemical waste is inspiring. The challenges faced to activate molecular oxygen for its use in oxidation reactions is due to its kinetically inert nature. However, if the organic substrate gets converted to a radical then its reaction with oxygen is a spin-allowed process. Among the other possibilities, the orbital overlap of oxygen with a suitable metal ion may help its activation through electron transfer from the metal. Such organic co-factors have been reviewed elsewhere and are beyond the scope of this review[11,12]. A major problem while using dioxygen in chemical transformation is that its reactivity is not easily controlled and often may lead to low selectivity and over-oxidation [13]. Nature has evolved an elegant solution to overcome the kinetic barrier of dioxygen activation by using transition metal incorporated in proteins, the so called 'metalloenzymes' [14-19]. Inorganic chemists have largely exploited the concept of nature by designing oxygen activation catalysts which act as small molecule mimics of the metalloenzymes and help to understand the mechanistic pathways. Using the knowledge of co-ordination chemistry, redox potential and electronic factors,[14,20-25] the enzymes donor

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Department Of Chemistry

REVIEW ARTICLE

TOPIC: Cobalt based models on Catechol
Oxidase: Biomimetic functional model and
mechanistic pathway

Submitted by- Ranita Konar

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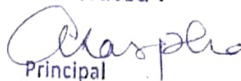
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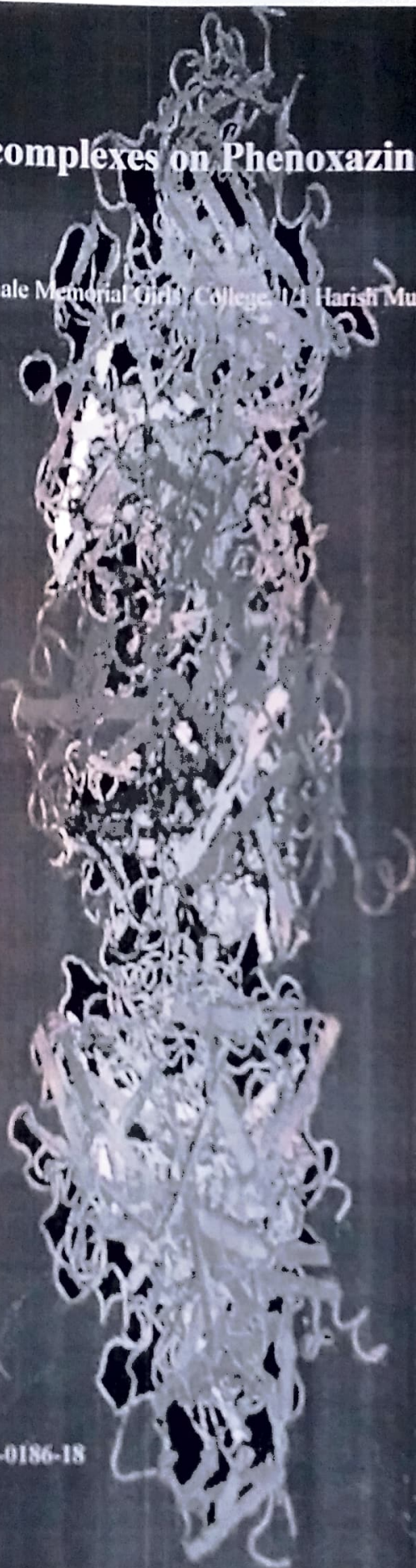
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Review

Mn-based model complexes on Phenoxazinone synthase

Moubani Mukherjee

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Abstract :

This review describes recent progress in modeling the active sites of Phenoxazinone Synthase that activate dioxygen to carry out several key reactions in nature. This review (up to 2021) is the continuation of the review done (up to 2015) by S. K. Dey and A. Mukherjee. The impetus to modeling of enzyme active sites comes from their potential to provide insight to the mechanistic pathways of the native enzymes, establish the role of that particular metal in the active site and to design better catalysts inspired by nature. Most of the metalloenzymes are capable of activating molecular oxygen due to the presence of the metal ions. The name phenoxazinone synthase (PHS, 2-aminophenol:oxygen oxidoreductase) is used for the enzyme catalysing the oxidative coupling of substituted *o*-aminophenols to produce phenoxazinones.

In this review we discuss the progress made so far in the area of phenoxazinone synthase modeling. The review shows that PHS has been widely attempted for modeling the active site. The biomimetic studies strongly suggest that among the various metal ions probed for modeling the catalytic activity of PHS, MnII/III based systems are so far the most promising candidates apart from the nature's choice Cu(II). PHS activity suggests the potential of such mimics may extend beyond the biological modeling and provide insight to the various possible mechanistic pathways that may be adapted by a model complex.

1. Introduction : Activation of molecular oxygen:

Oxidation reactions are fundamentally important component of organic synthesis and play an important role in rendering the desired functionality to the intermediates of valuable compounds such as pharmaceuticals, agrochemicals, and other fine chemicals. Molecular oxygen is an ideal oxidant because of its availability directly from air rendering it inexpensive and environmentally benign. The challenges faced to activate molecular oxygen for its use in oxidation reactions is due to its kinetically inert nature. A major problem while using dioxygen in chemical transformation is that its reactivity is not easily controlled and often may lead to low selectivity and over-oxidation. Nature has evolved an elegant solution to overcome the kinetic barrier of dioxygen activation by using transition metal incorporated in proteins, the so called 'metalloenzyme'. Inorganic chemists have largely exploited the concept of nature by designing oxygen activation catalysts which act as small molecule mimics of the metalloenzymes and help to understand the mechanistic pathways. Using the knowledge of co-ordination chemistry, redox potential and electronic factors, the enzymes donor sites are modeled with small molecule called ligands, which are then incorporated with metals to form complexes that are probed as structural and functional models[1].

Nature's choice and role of biomimetics:

Nature uses several metalloenzymes to catalyze the controlled and selective oxidation of organic compounds. The geometry and structural feature of enzyme active sites and the choice of incorporated metals are very diverse and fully optimized to the function of the proteins or enzymes. In addition it also takes into account the availability of the metal ion in

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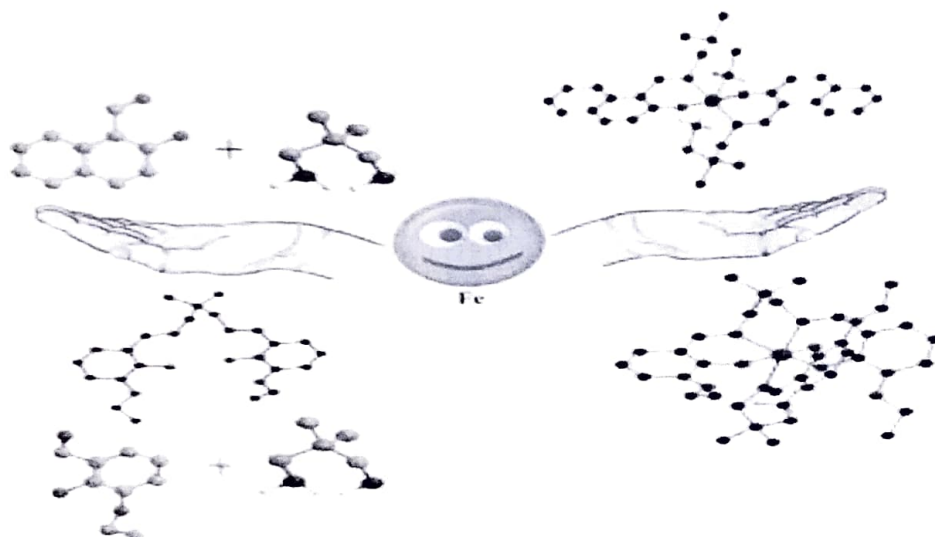
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REVIEW ON

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SEMESTER- VI

DISSERTATION : REVIEW REPORT

**PHENOXAZIONON SYNTHASE: BIOMIMETIC FUNCTIONAL
MODELS ON IRON COMPLEXES**

GOKHALE MEMORIAL GIRLS COLLEGE

DEPERTMENT OF CHEMISTRY

UNDER THE GUIDANCE OF : Dr. ANANGAMOHAN PANJA

SUBMITTED BY : RITHIKA BANERJEE

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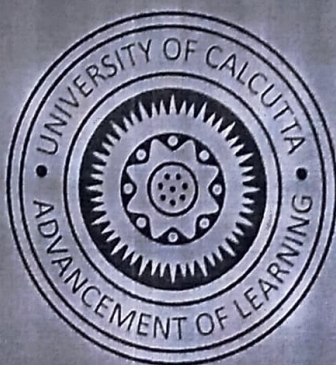
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ABSTRACT:

The impetus to modelling of enzyme active sites comes from their potential to provide insight to the mechanistic pathways of the native enzymes, establishing the role of that particular metal in the active site and to design better catalysts inspired by nature. Most of the metalloenzyme are capable of activating molecular oxygen due to the presence of the metal ions. Among the various metalloenzymes, phenoxazinone synthase (PHS) is an enzyme that is of interest for its oxidizing ability to generate phenoxazinone. In this review we discuss the progress made so far in the area of Fe-based models on phenoxazinone synthase enzyme. The studies on phenoxazinone synthase are quite detailed and the mechanistic pathways reasonably well disseminated as discussed here.

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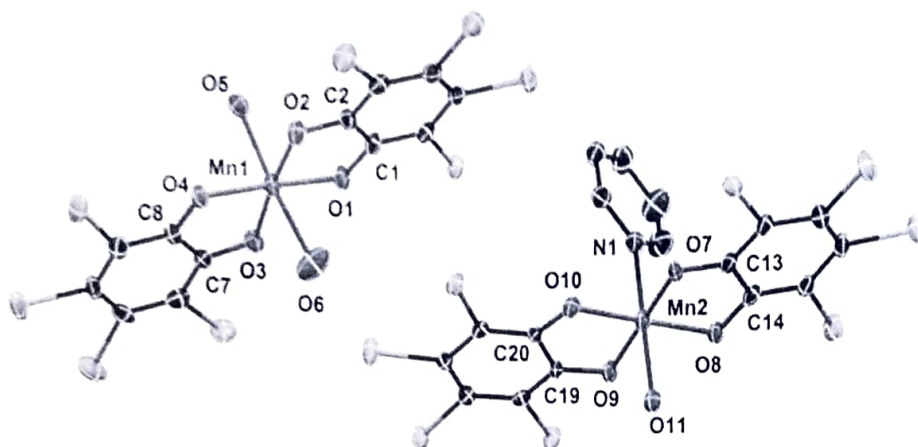
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Principal

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MANGANESE BASED CATECHOL OXIDASE: BIOMIMETIC FUNCTIONAL MODEL AND MECHANISTIC STUDIES

UNDER THE GUIDANCE OF:

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SUBMITTED BY: ANKITA DAS

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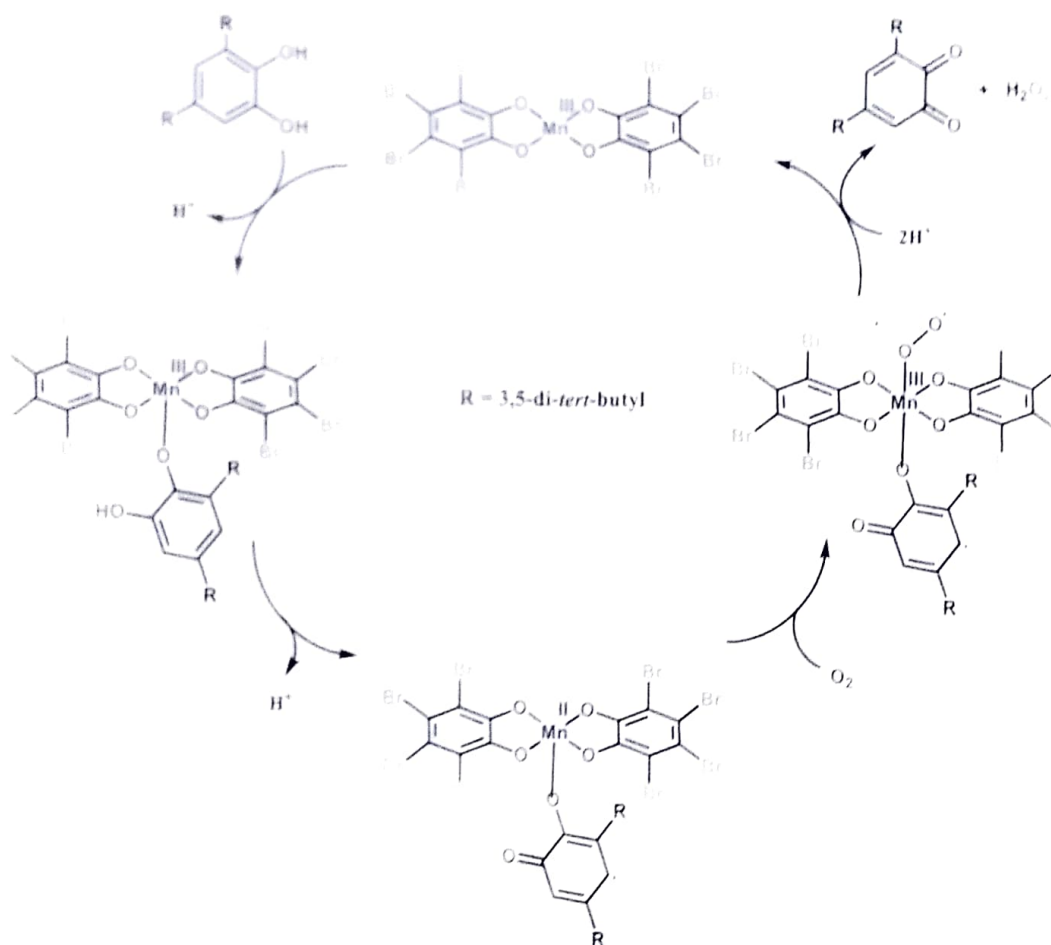
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REVIEW ON

MANGANESE BASED CATECHOL OXIDASE: BIOMIMETIC FUNCTIONAL AND MECHANISTIC STUDIES



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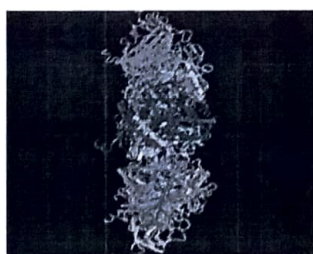
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Department of Chemistry

REVIEW ARTICLE

**TOPIC: COBALT BASED PHENOXAZINONE OXIDASE: BIOMIMETIC
FUNCTIONAL MODEL AND MECHANISTIC STUDIES**

UNDER THE GUIDANCE OF: DR. ANANGAMOHAN PANJA



SUBMITTED BY: TITAS NAG

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1. Abstract:

The impetus to modelling of enzyme active sites comes from their potential to provide insight to the mechanistic pathways of the native enzymes, establishing the role of that particular metal in the active site and to design better catalysts inspired by nature. Most of the metalloenzyme are capable of activating molecular oxygen due to the presence of the metal ions. Among the various metalloenzymes, phenoxazinone synthase (PHS) is an enzyme that is of interest for its oxidizing ability to generate phenoxazinone. In this review we discuss the progress made so far in the area of co-based models on phenoxazinone synthase enzyme. The studies on phenoxazinone synthase are quite detailed and the mechanistic pathways reasonably well disseminated as discussed here.

2. Introduction:

2.1 Activation of molecular oxygen

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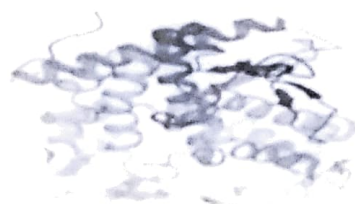
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Review article on
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FUNCTIONAL MODEL AND MECHANISTIC PATHWAY



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C. Karpale

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ABSTRACT

The impetus to modeling of enzyme active sites comes from their potential to provide insight to the mechanistic pathways of the native enzymes, establish the role of that particular metal in the active site and to design better catalysts inspired by nature. Most of the metalloenzymes are capable of activating molecular oxygen due to the presence of the metal ions. Among the various metalloenzymes, in this project we discuss about catechol oxidase (CO) which is of interest for the oxidizing ability to generate o-quinones. The review shows that the enzymes CO have been widely attempted for modeling the active site. The model of CO being capable of generating semiquinones type radicals; it also have been probed for oxidative C-C bond coupling in sterically hindered phenol.

INTRODUCTION

I. Activation of Molecular oxygen-

Oxidation reactions are fundamentally important component of organic synthesis and play an important role in rendering the desired functionality to the intermediates of valuable compounds such as pharmaceuticals, agrochemicals, and other fine chemicals. For economic and environmental reasons, the oxidation processes of bulk chemical industries predominantly involve the use of molecular oxygen as the primary oxidant. Molecular oxygen is an ideal oxidant because of its availability directly from air rendering it inexpensive and environmentally benign. However, the application of oxidation reactions in scaled-up synthesis is limited due to the use of heavy metals, thermal hazards, and moderate chemo selectivity for highly functionalized compounds in most oxidation reactions. Classical oxidation methods with stoichiometric quantities of inorganic oxidants are toxic and enrich the environmental pollution. That is why oxidations using catalytic amount of activator which can activate molecular oxygen with minimum chemical waste is inspiring. The challenges faced to activate molecular oxygen for its use in oxidation reactions is due to its kinetically inert nature. The reaction of molecular oxygen with organic substrates do not take place under ambient conditions as typical organic molecules in general posses singlet ground state and their reaction with oxygen is spin forbidden. However, if the organic substrate gets converted to a radical then its reaction with oxygen is a spin-allowed process. Among the other possibilities, the orbital overlap of oxygen with a suitable metal ion may help its activation through electron transfer from the metal. Electron transfer may also happen through orbital overlap with potent

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REVIEW ARTICLE ON

CATECHOL OXIDASE: STUDY ON BIOMIMETIC FUNCTIONAL NI BASED MODELS

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CATECHOL OXIDASE: STUDY ON BIOMIMETIC FUNCTIONAL NI BASED MODELS

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Semester-6 Dissertation Review Article

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Yours truly,

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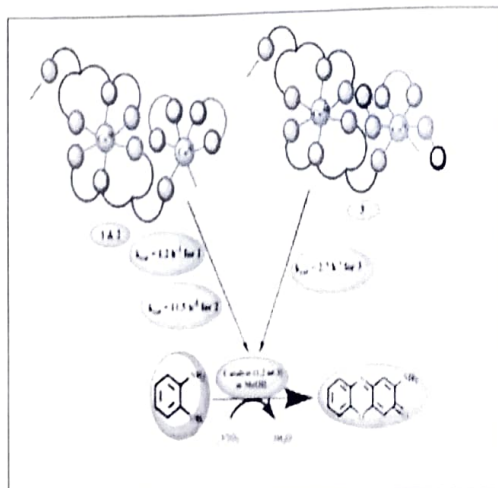
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A Review Report Submitted on *Phenoxazinonesynthase: Biomimetic functional Models and mechanistic studies*



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Abstract:

Biomimetics is the study of nature and natural phenomena to understand the principle of underlying mechanisms, to obtain ideas from nature, and to apply concepts that may benefit science. Nature uses several metalloenzymes to catalyze the controlled and selective oxidation of organic compounds. The geometry and structural feature of enzyme active sites and the choice of incorporated metals are very diverse and fully optimized to the function of the proteins or enzymes. In addition it also takes into account the availability of the metal ion in environment. Establishing the correlation of the geometric and electronic structure with function is one of the main objectives of the bioinorganic chemists. The activation of dioxygen on metal sites requires the availability of different accessible redox states. Metalloenzymes capable of dioxygen activation consist mainly of enzymes with copper, iron or manganese active sites. A wide variety of different mono- or multinuclear iron and copper enzymes has been discovered and catalyzes major biological transformations. Among the various metalloenzymes phenoxazinone synthase (PHS) is of interest for oxidizing ability to generate phenoxazinones. In this review we discuss the progress made so far in the area of phenoxazinone synthase modeling based on Cu(II) metal centre. The progress on phenoxazinone synthase and its mechanistic pathway is rather poor and has lot of scope for improvement. The review shows that PHS has been widely attempted for modeling the active site. The biomimetic studies strongly suggest that among the various metal ions probed for modeling the catalytic activity of PHS, systems are so far the most promising candidate is Cu(II) . Many researchers added various ligands and making changes to the cluster for improvement in synthetic production. PHS activity suggests the potential of such mimics may extend beyond the biological modeling and provide insight to the various possible mechanistic pathways that may be adapted by a model complex.

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