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

CU ROLL NO.: 193013-11-0003

CU REGISTRATION NO.: 013-1211-0239-19

Authenticated

Principal

Gokhale Memorial Girls' College

05 JAN 2023

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 phenoxazionone synthase enzyme. The studies on phenoxazinone synthase are quite detailed and the mechanistic pathways reasonably well disseminated as discussed here.

ZINC BASED CATECHOL OXIDASE: BIOMIMETIC FUNCTIONAL MODEL AND MECHANISTIC PATHWAY

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

Course: CEMA DSE – B4 (Dissertation)

CU Roll No. – 193013-11-0004

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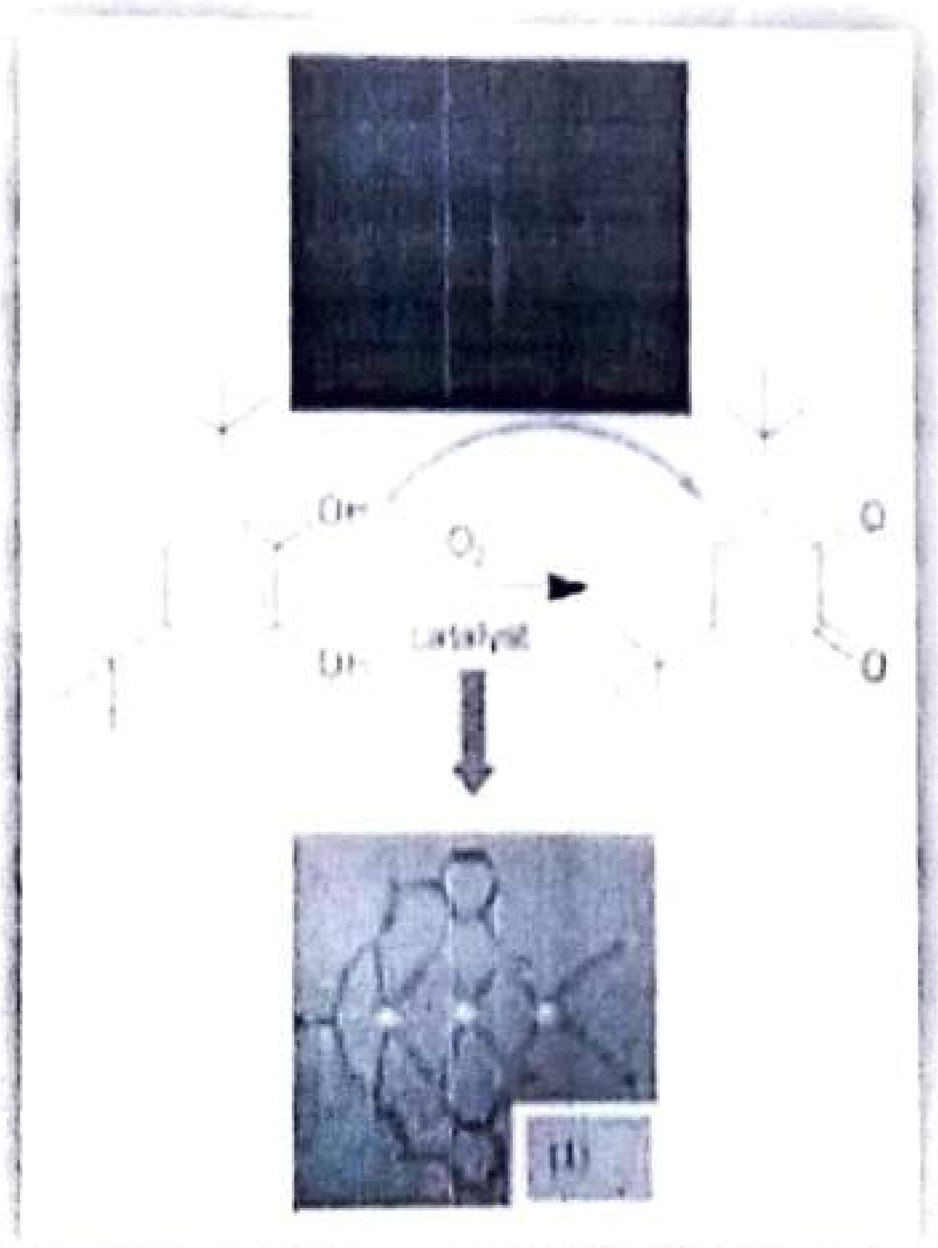
05 JAN 2023

ABSTRACT

A new trinuclear zinc (II) complex, $[Zn_3(L)(NCS)_2](NO_3)_2\cdot CH_3OH\cdot H_2O$ (**1**), of a (N, O)-donor compartmental Schiff base ligand (H_2L = 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 Å, b = 10.849 Å, c = 18.339 Å, with unit cell volume is 2179.713 $(Å)^3$. 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 $[Zn_2(L)(3,5\text{-}DTBC)]$. 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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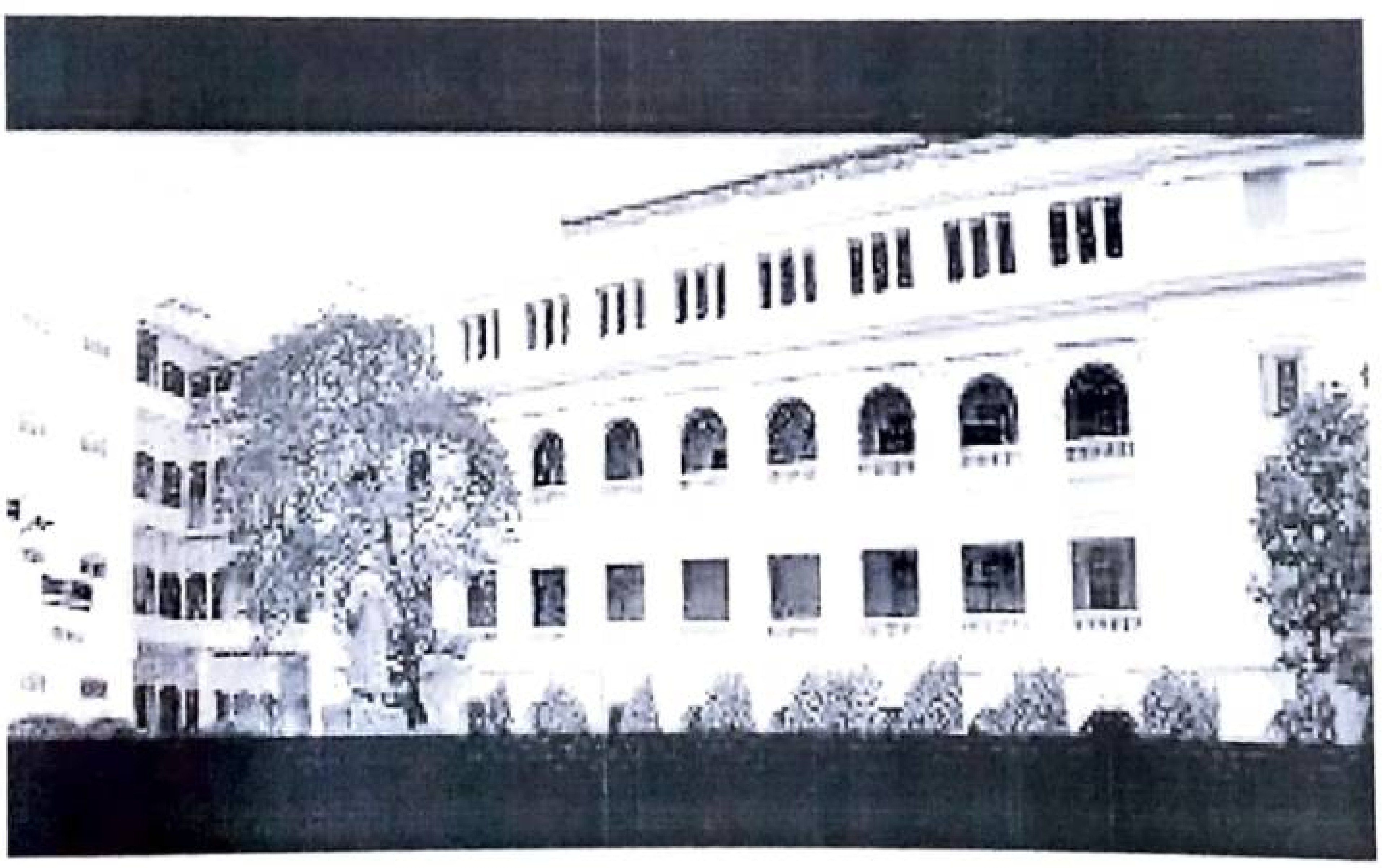

REVIEW ARTICLES

GOKHALE MEMORIAL GIRLS' COLLEGE

1/1,Harish Mukherjee Rd,Gokhale Road,Bhawanipore,Kolkata,West Bengal700020

DEPARTMENT OF CHEMISTRY

TOPIC

Phenoxazinone sythase activity of a Mn based complex

SUBMITTED BY

NAME:SRIDIPA MANDAL

REGISTRATION NO:013-1214-0232-19

CU ROLL NO:193013-11-0005

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05 JAN 2023

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 (upto2015) 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-amiophenol 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 biommimetic 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 containg copper.It acts as 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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UNDER THE GUIDANCE OF:

DR. ANANGAMOHAN PANJA

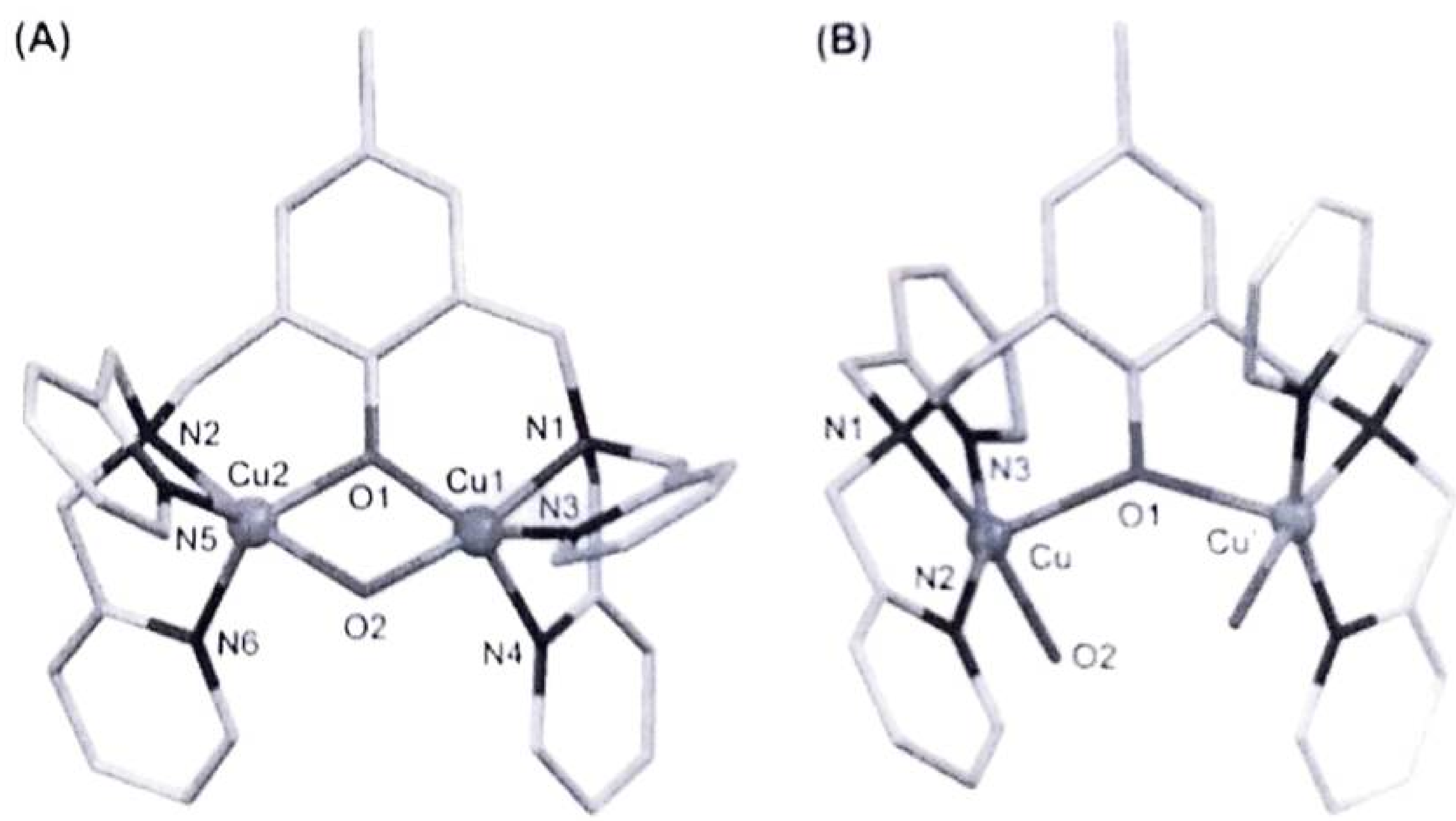
SUBMITTED BY: NAJNIN MANDAL

CU ROLL NO:193013-11-0006

CU REGISTRATION NO: 013-1215-0233-19

REVIEW ON

COPPER BASED CATECHOL OXIDASE : BIOMIMETIC FUNCTIONAL AND MECHANISTIC STUDIES



Gokhale Memorial Girls' College

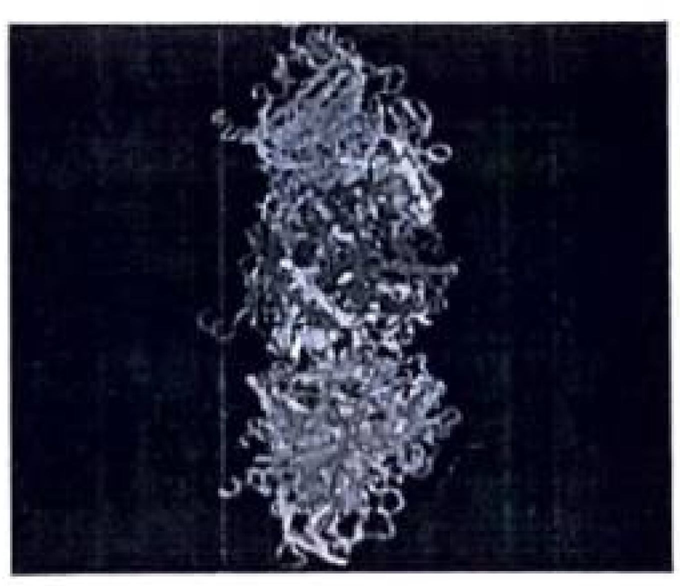
1/1, Harish Mukherjee Rd, Kolkata, West Bengal 700020

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

CU ROLL NO.: 193013 – 11- 0103

CU REG. NO.: 026 – 1215 -0082 - 18

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 phenoxazionone 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 componentof organic synthesis and play an important role in rendering thedesired functionality to the intermediates of valuable compoundssuch 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 synthesisis limited due to the use of heavy metals, thermal hazards, andmoderate chemoselectivity for highly functionalized compounds inmost oxidation reactions[9,10]. Classical oxidation methods withstoichiometric quantities of inorganic oxidants are toxic and enrichthe environmental pollution. That is why oxidations using catalyticamount of activator which can activate molecular oxygen withminimum chemical waste is inspiring. The challenges faced to activate molecular oxygen for its use in oxidation reactions is due toits kinetically inert nature. However.if the organic substrate gets converted to a radical then its reaction with oxygenis a spin-allowed process. Among the other possibilities, the orbitaloverlap of oxygen with a suitable metal ion may help its activationthrough electron transfer from the metal. Such organic co-factors have been reviewedelsewhere 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 oftenmay lead to low selectivity and over-oxidation [13]. Nature hasevolved an elegant solution to overcome the kinetic barrier ofdioxygen activation by using transition metal incorporated in proteins, the so called 'metalloenzymes' [14-19]. Inorganic chemists have largely exploited theconcept of nature by designing oxygen activation catalysts whichact as small molecule mimics of the metalloenzymes and helpto 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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Gokhale Memorial Girls' College

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

Department Of Chemistry

REVIEW ARTICLE

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

Submitted by- Ranita Konar

CU Reg. No: 013-1211-0167-18

CU Roll No: 183013-11-0004

Authenticated .
Principal
Gokhale Memorial Girls' College
05 JAN 2023

I N D E X

CONTENTS

Review

Mn-based model complexes on Phenoxazinone synthase

Moubani Mukherjee

Department of Chemistry, Gokhale Memorial Girls' College, 1/1 Harish Mukherjee Road, Gokhale Road, Kol-20

Name- Moubani Mukherjee

Registration number: 013-1211-0186-18

Roll number: 183013-11-0005

Content : | **Page**

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 transfomation 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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SUBMITTED BY: SABNAM KHATUN

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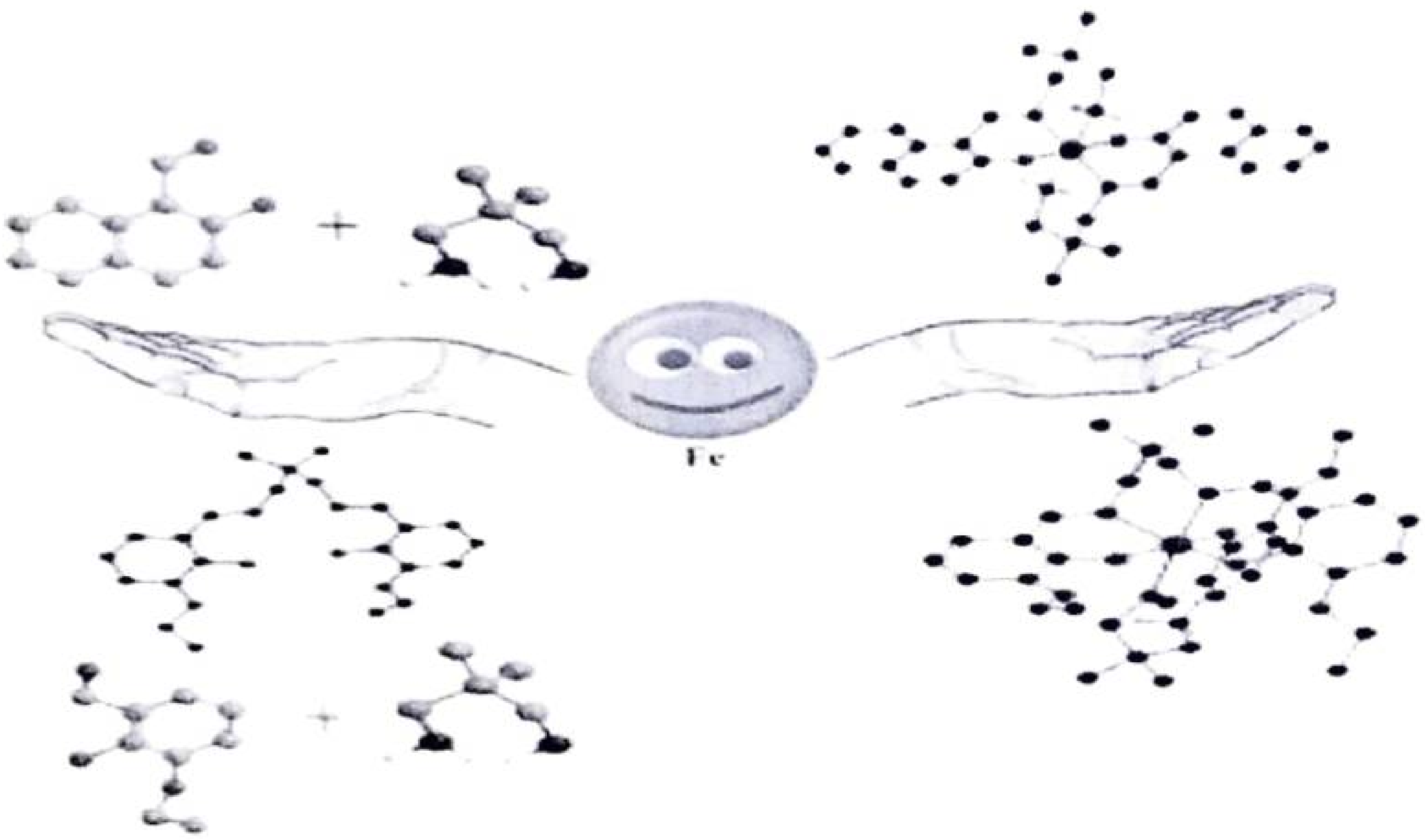

REVIEW ON

FERROUS BASED CATECHOL OXIDASE:

BIOMIMETIC FUNCTIONAL AND MECHANISTIC STUDIES

UNIVERSITY OF CALCUTTA

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CHEMISTRY BSc. (HONS)

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

CU ROLL NO. : 183013-11-0001

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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 phenoxazionone synthase enzyme. The studies on phenoxazinone synthase are quite detailed and the mechanistic pathways reasonably well disseminated as discussed here.

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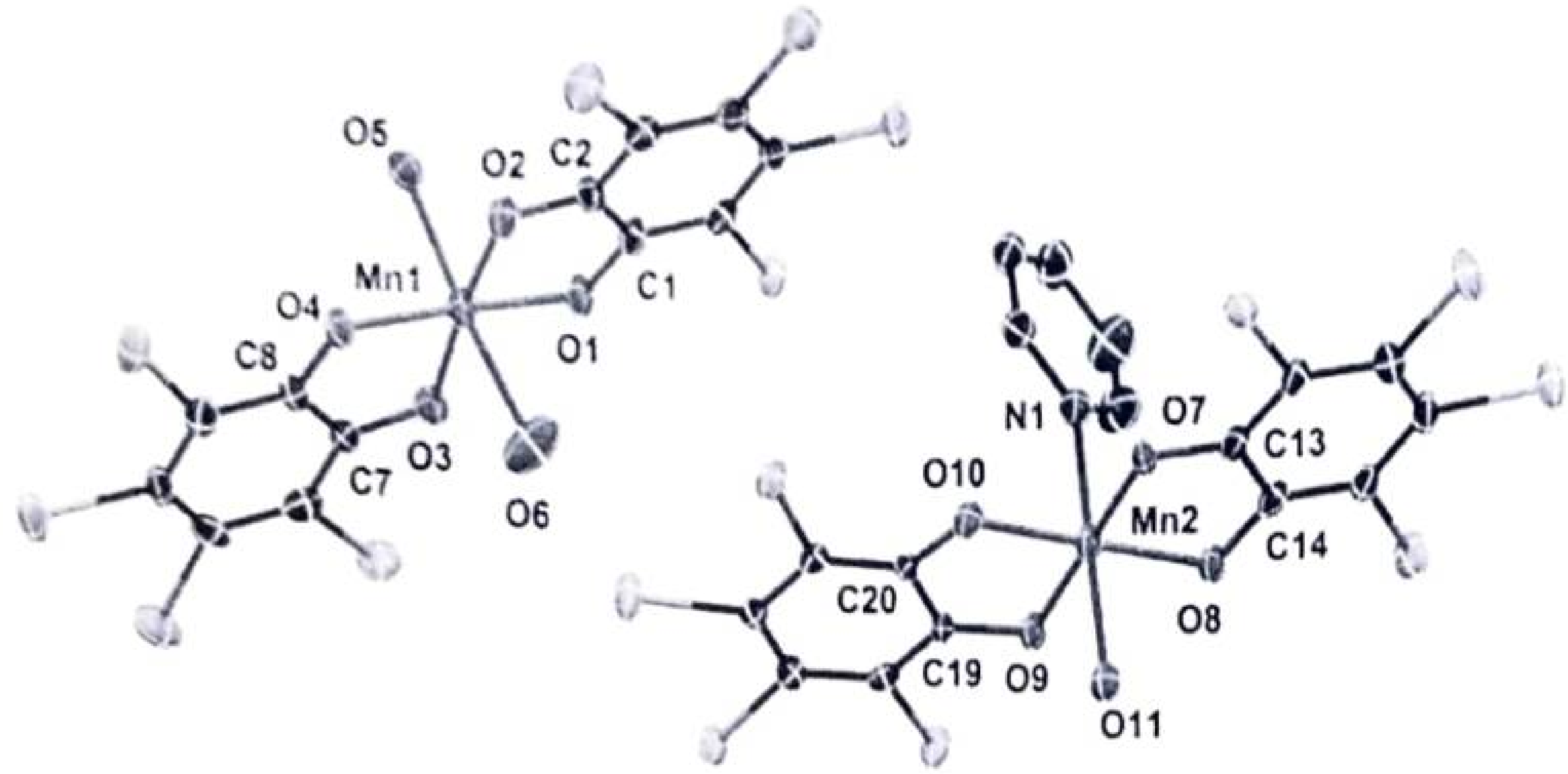

MANGANESE BASED CATECHOL OXIDASE: BIOMIMETIC FUNCTIONAL MODEL AND MECHANISTIC STUDIES

UNDER THE GUIDANCE OF:

Dr. ANANGAMOHAN PANJA

SUBMITTED BY: ANKITA DAS

CU ROLL NO.: 183013-11-0002

CU REGISTRATION NO.: 013-1211-0079-18

DEPARTMENT OF CHEMISTRY

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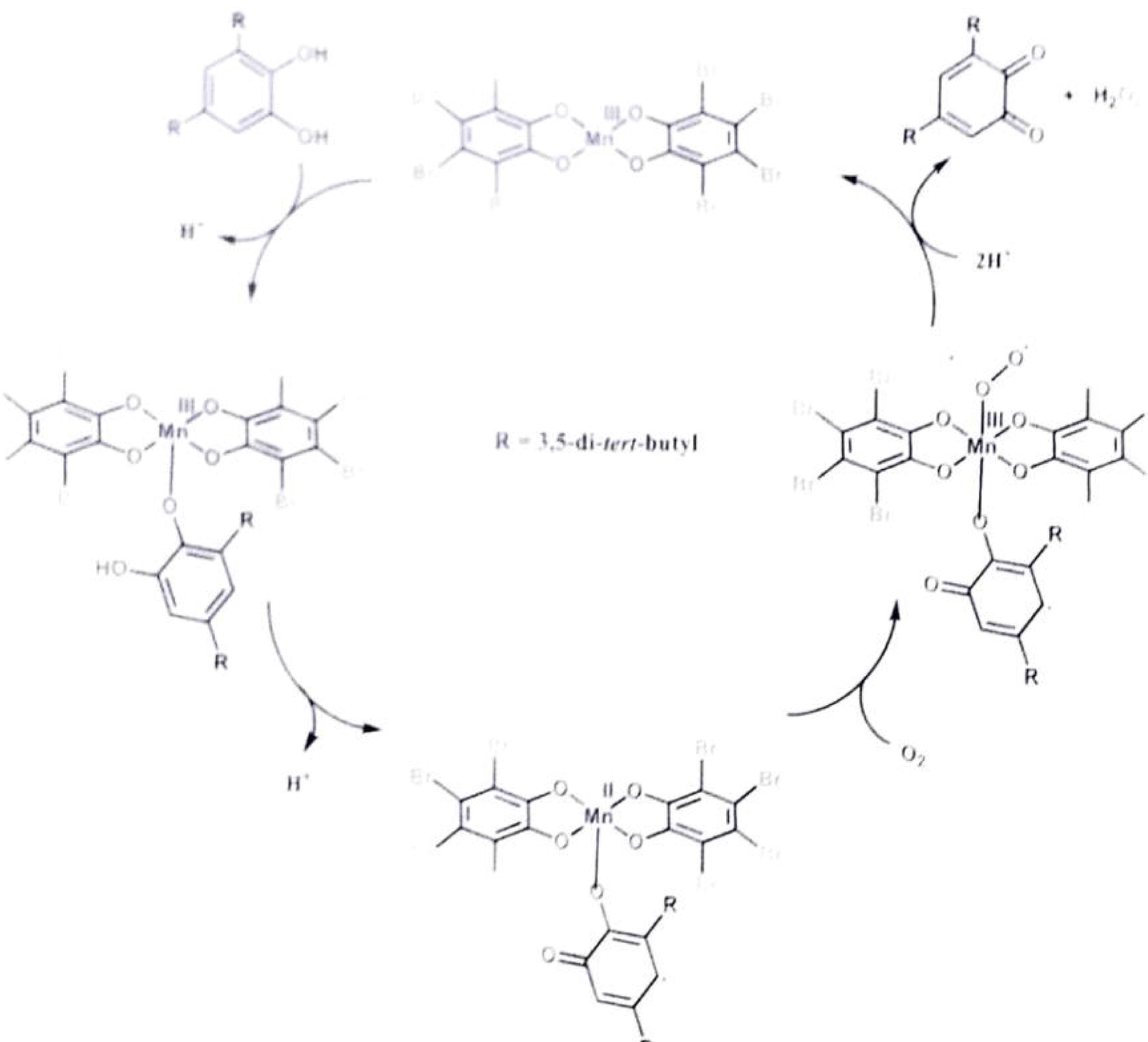
REVIEW ON

MANGANESE BASED CATECHOL OXIDASE: BIOMIMETIC FUNCTIONAL AND MECHANISTIC STUDIES



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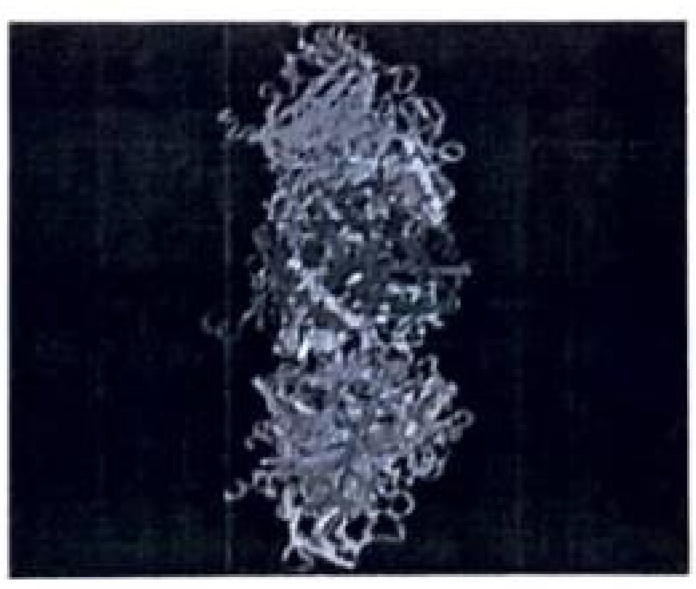
Department of Chemistry

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 phenoxazionone synthase enzyme. The studies on phenoxazinone synthase are quite detailed and the mechanistic pathways reasonably well disseminated as discussed here.

2. Introduction:

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Review article on

ZINC BASED CATECHOL OXIDASE: BIOMIMEMTIC FUNCTIONAL MODEL AND MECHANISTIC PATHWAY

GOKHALE MEMORIAL GIRLS' COLLEGE

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UNDER THE GUIDANCE OF DR ANANGAMOHAN PANJA

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INDEX

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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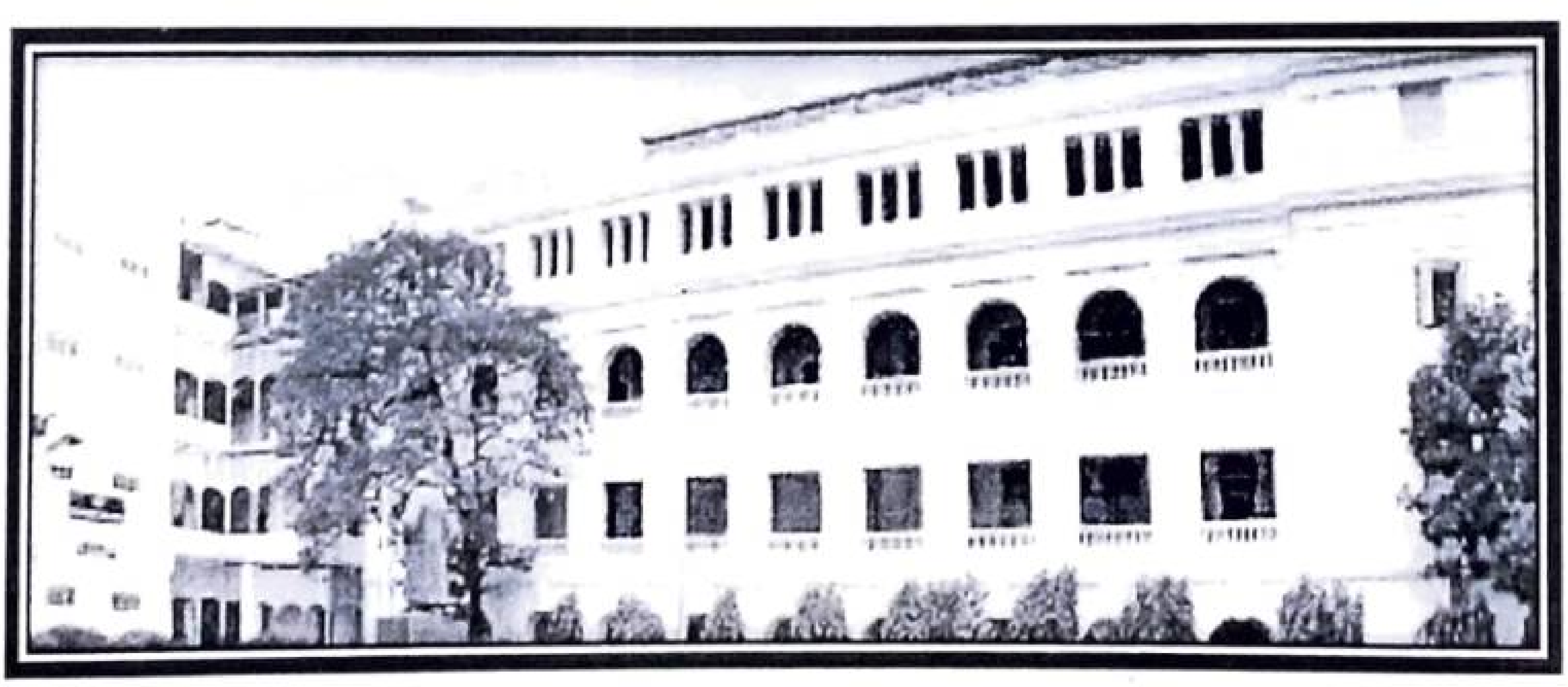

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NAAC ACCREDITED (2nd Cycle)

GRADE B (2.79 CGPA) 2015

DEPARTMENT OF CHEMISTRY

DSE-B4: DISSERTATION

REVIEW ARTICLE

SUBMITTED BY : PRIYA KUMARI

CU Registration No: 013-1211-0253-18

CU Roll No.: 183013-11-0007

College Roll No. : BSCH/18/0012

ACKNOWLEDGEMENT

IT GIVES ME TREMENDOUS PLEASURE IN ACKNOWLEDGING THE VALUABLE ASSISTANCE EXTENDED TO ME IN THE SUCCESSFUL COMPLETION OF THIS REVIEW.

IT FEELS GREAT PLEASURE TO EXPRESS MY DEEP SENSE OF GRATITUDE TO DR. ANANGAMOHAN PANJA, ASSISTANT PROFESSOR, DEPARTMENT OF CHEMISTRY, GOKHALE MEMORIAL GIRLS' COLLEGE FOR HIS EXCELLENT GUIDANCE, CONSTANT ENCOURAGEMENT AND KEEN INTEREST THROUGH THE PROCESS OF THIS REVIEW PROJECT. HIS VALUABLE SUGGESTION AND ACTIVE HELP WERE THE KEY SOURCES OF INSPIRATION TO ME.

I WOULD ALSO LIKE TO EXTEND MY GRATITUDE TO PRINCIPAL MA'AM DR. ATASHI KARPHA FOR PROVIDING ME WITH ALL THE FACILITIES REQUIRED. AND EXTENDED THANKS TO OUR RESPECTED PROFESSORS OF THE DEPARTMENT OF CHEMISTRY DR. GAUTAM MAHATO, DR. ARIJIT DEY AND SRI SHANTANU SAMANTA FOR THEIR SUPPORT AND ENCOURAGEMENT.

I MUST EXPRESS MY DEEPEST REGARD TO MY PARENTS AND FELLOW CLASSMATES FOR THEIR CONTINUOUS ENCOURAGEMENT AND SUPPORT.

DATE : 01 – 08 – 2021

Priya Kumari

BSCH/18/0012

Reg. No: 013-1211-0253-18

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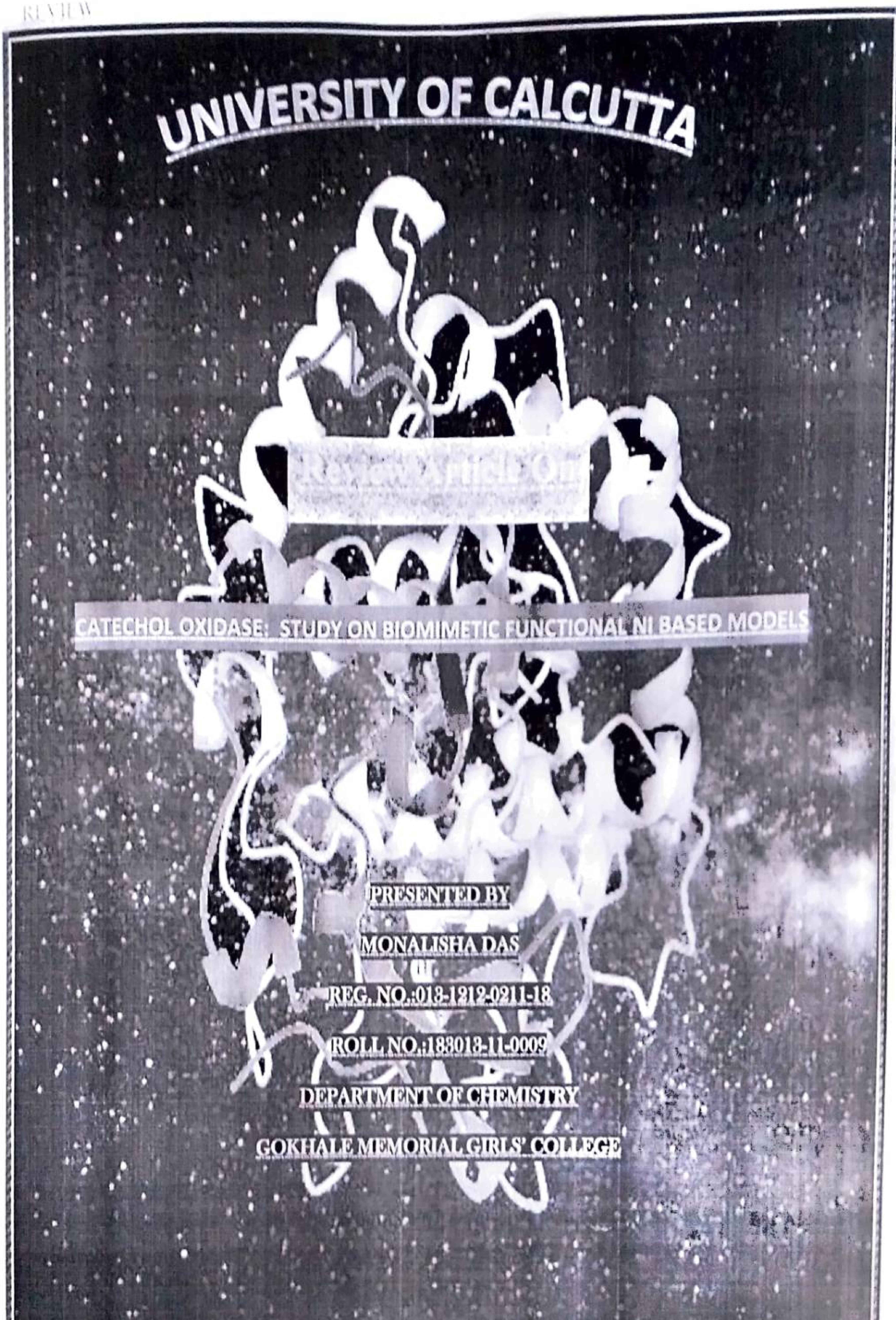

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Review Article On

CATECHOL OXIDASE: STUDY ON BIOMIMETIC FUNCTIONAL NI BASED MODELS

PRESENTED BY

MONALISHA DAS

OF

REG. NO.:013-1212-0211-18

ROLL NO.:183013-11-0009

DEPARTMENT OF CHEMISTRY

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CATECHOL OXIDASE: STUDY ON BIOMIMETIC FUNCTIONAL NI BASED MODELS

*Monalisha Das** **Department of Chemistry, Gokhale Memorial Girls' College, 1/1 Harish Mukherjee Road,Kol-20**

Semester-6 Dissertation Review Article

Under supervision of Dr. Ananghamohan Panja

SUBMITTED BY:

Monalisha Das

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University Registration No.-013-1212-0211-18

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05 JAN 2023

Acknowledgment

I would like to take opportunity to express my deep sense of gratitude and special thanks to Dr. Anangamohan Panja, Assistant Professor, Department Of Chemistry, Gokhale Memorial Girls' College who gave me this golden opportunity to do this unique as well as wonderful review work on topic based on "Catechol oxidase study on biomimetic fuctional of Ni based model" and without whom this review work would not be succeded smoothly. He helped me a lot for doing research and I came to know several new things. It was a completely new topic for me but he encouraged us a lot to accept this challenging work and have different marvellous experience. He made me enthusiastic for my future research work also by his tremendous positive encouragement.

I would also like to extend my heartfelt gratitude to respected principal Dr. Atashi Karpha and all respected teachers of Department of Chemistry, Dr. Goutam Mahata, Dr. Arijit De and Sir Santanu Samanta for their strong suppert and encouragement.

Atlast, I would like to thank my parents and my all well-wishers for inexhaustible source of inspiration and wonderful suggestions for giving it fine touch of completion.

Date: 25.07.2021

Monalisha Das

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Contents:

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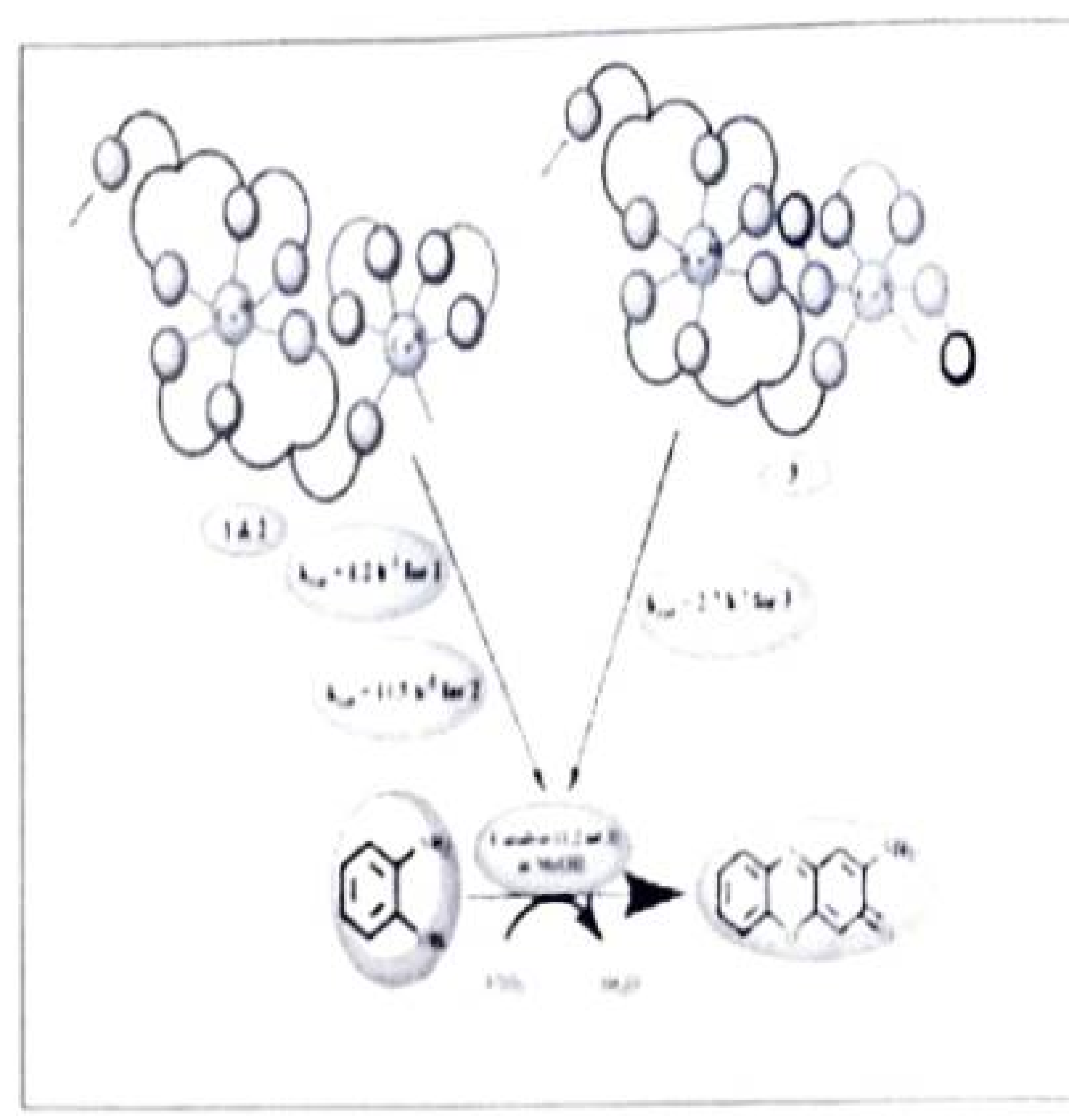
A Review Report Submitted on

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. Metalloen-zymes 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.