ELECTROCATALYTIC WATER OXIDATION ACTIVITY BY MOLECULAR COPPER AND COBALT COMPLEXES AND MECHANISTIC INVESTIGATIONS

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Electrocatalytic Water Oxidation Activity by Molecular Copper and Cobalt Complexes and Mechanistic Investigations

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Dedicated to my beloved Teachers
and
Parents

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CERTIFICATE FROM THE SUPERVISOR

This is to certify that the thesis entitled *"Electrocatalytic Water Oxidation Activity by Molecular Copper and Cobalt Complexes and Mechanistic Investigations*," submitted by Ms. Moumita Bera to the Indian Institute of Technology Delhi for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by her. Ms. Moumita Bera worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge, has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

Date: 31-07-2023

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ABSTRACT

The thesis entitled *"**Electrocatalytic Water Oxidation Activity by Molecular Copper and Cobalt Complexes and Mechanistic Investigations**"* deals with the development and characterization of molecular electrocatalysts based on 3d late transition metal complexes for the water oxidation reaction. In the WO reaction, removal of four electrons and four protons is needed from two water molecules to generate one molecule of dioxygen, four equiv. of protons and four equiv. of electrons, $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$. The reaction is thermodynamically uphill ($E^0 = 1.23$ V vs. NHE at pH = 0) and requires high overpotential to drive. With suitable ligand support, the mentioned metal ions can reach higher oxidation states, required for the removal of electrons and protons from H_2O molecules. However, accessibility of high-valent $M^{n+}O$ species for the late-transition metal (LTM) ions (Co, Ni, and Cu) is not easy because of unavailability of empty *d* orbitals required for the formation of oxo-metal multiple bonds. Nevertheless, a LTM ion supported by a redox-active ligand can satisfy the oxidative equivalents required for the oxidation of water by reversible ligand oxidation reactions. Recently, a couple of WO electrocatalysts based LTM ions of nitrogen rich ligands are reported in the literature, where the redox-active ligands were shown to assist electrocatalytic WO reactions at a relatively low overpotentials. Therefore, LTM electrocatalysts supported by redox-active ligands are a promising strategy for the development of electrocatalytic WO reactions. We envisioned that redox-active and electron rich ligands containing alkoxide donor atoms might enable easy access to high-valent metal complexes required for WO reactions. Here we explored the electrocatalytic water oxidation activity of molecular copper and cobalt complexes. Further, we focused attention on the spectroscopic characterization and reactivity studies of the reaction intermediates formed in the water oxidation pathway.

Chapter 1. Introduction

This chapter describes a brief overview of electrocatalytic water oxidation of molecular 3d transition metal complexes. The chapter also focuses on the characterization of reaction intermediates which were isolated and characterized in the literature. In addition, the introduction chapter describes the present challenges yet to overcome to develop efficient electrocatalysts for water splitting reactions.

Chapter 2. Electrocatalytic Water Oxidation Activity of Molecular Copper Complexes: Effect of Redox Active Ligands

Two molecular copper (II) complexes, $(NMe_4)_2[Cu^{II}(L^1)]$ (**1**) and $(NMe_4)_2[Cu^{II}(L_2)]$ (**2**), ligated by N2O2 donor set of ligands (L^1 = *N*,*N'*-(1,2-phenylene)bis(2-hydroxy-2-methylpropanamide) and L^2 = *N*,*N'*-(4,5-dimethyl-1,2-phenylene)bis(2-hydroxy-2-methylpropanamide)) have been synthesized and thoroughly characterized. Electrochemical study of **1** and **2** in a carbonate buffer at pH 9.2 revealed a reversible copper centered redox couple, followed by two ligand-based oxidation events and catalytic water oxidation. Results from theoretical electronic structure investigation corroborated well with the observed step-wise ligand-centered oxidation process. One-electron oxidized species of **1**, $(NMe_4)[Cu^{III}(L^1)]$ (**3**), was isolated and characterized. The study demonstrates the importance of redox-active ligands on the development of molecular late-transition-metal electrocatalysts for WO reactions. The energetically favorable mechanism has been established through the theoretical calculation of stepwise reaction energies, which nicely explains the experimentally observed electron transfer events.

Chapter 3. Structural and Spectroscopic Characterization of Copper(III) Complexes and Subsequent One-Electron Oxidation Reaction and Reactivity Studies

The formation of Cu^{III} species is often invoked as the key intermediate in Cu-catalyzed organic transformation reactions. In this study, we synthesized Cu^{II} (**2**) and Cu^{III} (**4**) complexes supported by a bisamidate-bisalkoxide ligand consisting of an *ortho*-phenylenediamine (o-PDA) scaffold and characterized them through an array of spectroscopic techniques. X-ray structures, the prominent shift of $1s \rightarrow 4p$ and $1s \rightarrow 3d$ transition energy in the XANES data, and theoretical studies implies **4** to be a genuine Cu^{III} complex. In addition, in order to get a clear picture of the effect of redox non-innocent o-PDA moiety on the Cu–N/O distances at the +III oxidation state of Cu, complex **6** has been synthesized by using a redox innocent *trans*-1,2-diaminocyclohexane moiety replaces the o-PDA scaffold and exhibited almost identical metrical parameters compared to **4**, denoting that the redox-active feature of the o-PDA backbone is not activated in **4**. Further, One-electron oxidation reaction of **4** further resulted in the formation of a ligand-oxidized Cu complex (**4a**), which was characterized in-depth. Reactivity studies of species **4** and **4a** were explored towards the activation of the C–H/O–H bonds. A bond dissociation free energy (BDFE) value of ~69 kcal/mol was estimated for the O–H bond of the Cu^{II} complex formed upon transfer of hydrogen atom to **4**. The study represents a thorough spectroscopic characterization of high-valent Cu complexes and sheds light on the PCET reactivity studies of Cu^{III} complexes.

In Chapter 4. Effect of Structural Flexibility on the Electrocatalytic Water Oxidation of Molecular Copper Complexes at Neutral Aqueous Medium

The development of molecular copper electrocatalyst for water oxidation reactions is an important topic of research. In this work, we designed and synthesized molecular copper complexes (**7** and **8**) supported by bis-pyridine-bis-oxime ligands to understand the effect of ligand architectures on the electrocatalytic water oxidation activity. Complex **7** is ligated by N-phenyl-N-(pyridin-2-yl) pyridin-2-amine scaffold, carrying flexible ligand architecture. Complex **8** is supported by bipyridine based ligand scaffold, comprising of a more rigid structure, as is evident from the X-ray structure of the Cu complexes. Electrocatalytic water oxidation activity of the copper complexes were examined, which revealed a higher catalytic reaction rate of **7** than **8**. The apparent higher reactivity of **7** is likely because of the short O–O distance between two oxime oxygen atoms, which favors formation of copper-based reaction intermediates in the transition state. In addition, ligand centered redox event was observed in **7** assists the WO reaction at a low overpotential. **8**, licking the redox-active aniline moiety showed WO at a higher overpotential and lower TOF compared to **7**.

Chapter 5. Characterization of Reaction Intermediates Involved in Water Oxidation Reaction of a Molecular Cobalt Complex

Molecular Cobalt(III) complexes of bis-amidate-bis-alkoxide ligands, $(Me_4N)[Co^{III}(L^1)]$ (**9**) and $(Me_4N)[Co^{III}(L^2)]$ (**10**) are synthesized and assessed through a range of characterization techniques. Electrocatalytic water oxidation activity of the Co complexes in a 0.1 M phosphate buffer solution revealed a ligand-centered $2e^-/1H^+$ transfer event at 0.99 V followed by catalytic water oxidation (WO) at an onset overpotential of 450 mV. By contrast, **10** reveals a ligand-based oxidation event at 0.9 V and WO onset overpotential of 430 mV. Constant potential electrolysis study and rinse test experiments confirm the homogeneous nature of the Co complexes during WO. The mechanistic investigation further shows a pH-dependent change in the reaction pathway. On the one hand, below pH 7.5, two consecutive ligand-based oxidation events result in the formation of a $Co^{III}(L^{2-})(OH)$ species which, followed by a proton-coupled electron transfer reaction, generates a $\mathrm{Co^{IV}(L^{2-})(O)}$ species that undergoes water nucleophilic attack to form the O–O bond. On the other hand, at higher pH, two ligand-based oxidation processes merge together and result in the formation of a $\mathrm{Co^{III}(L^{2-})(OH)}$ complex, which reacts with $\mathrm{OH^{-}}$ to yield the O–O bond. The ligand coordinated reaction intermediates involved in the WO reaction are thoroughly studied through an array of spectroscopic techniques, including UV-vis absorption spectroscopy, Electron Paramagnetic Resonance, and X-ray absorption spectroscopy. A mononuclear $\mathrm{Co^{III}(OH)}$ complex supported by the one-electron oxidized ligand, $\mathrm{[Co^{III}(L^{3-})(OH)]^{-}}$, a formal $\mathrm{Co^{IV}(OH)}$ complex, has been characterized, and the compound was shown to participate in the hydroxide rebound reaction, which is a functional mimic of Compound II of Cytochrome P450.

सारांश

"***आणविक कॉपर और कोबाल्ट कॉम्प्लेक्स और यांत्रिक जांच द्वारा इलेक्ट्रोकैटेलिटिक जल ऑक्सीकरण गतिविधि"*** नामक थीसिस पानी ऑक्सीकरण प्रतिक्रिया के लिए 3 डी धातु परिसरों के आधार पर कुशल इलेक्ट्रोकेटेलिस्ट के विकास और लक्षण वर्णन से संबंधित है। डब्ल्यूओ प्रतिक्रिया में, डाइऑक्सीजन 2 एच 2 ओ ओ 2 → + 4 एच + 4 ई के एक अणु को उत्पन्न करने के लिए दो पानी के अणुओं से चार इलेक्ट्रॉनों और चार प्रोटॉन को हटाने की आवश्यकता होती$^{-}$ है, थर्मोडायनामिक रूप से ऊपर है (*ई*^{0} = 1.23 वी बनाम एनएचई पीएच = 0 पर)। उपयुक्त लिगैंड समर्थन के साथ, उल्लिखित धातु आयन उच्च ऑक्सीकरण अवस्थाओं (Mn $^{+}$ O प्रजाति (n = IV-VII)) तक पहुंच सकते हैं, जो H2 O अणुओं से इलेक्ट्रॉनों को हटाने के लिए आवश्यक हैं। हालांकि, ऑक्सो-मेटल मल्टीपल बॉन्ड के गठन के लिए आवश्यक खाली *डी* ऑर्बिटल्स की अनुपलब्धता के कारण लेट-ट्रांजिशन मेटल (एलटीएम) आयनों (सीओ, नी और क्यू) के लिए उच्च-वैलेंट एमएन $^{+}$ ओ प्रजातियों की पहुंच आसान नहीं है। फिर भी, रेडॉक्स-सक्रिय लिगैंड द्वारा समर्थित एक एलटीएम आयन प्रतिवर्ती लिगैंड ऑक्सीकरण प्रतिक्रियाओं द्वारा पानी के ऑक्सीकरण के लिए आवश्यक ऑक्सीडेटिव समकक्षों को संतुष्ट कर सकता है। हाल ही में, नाइट्रोजन समृद्ध लिगेंड के डब्ल्यूओ इलेक्ट्रोकेटेलिस्ट आधारित एलटीएम आयनों के एक जोड़े को साहित्य में रिपोर्ट किया गया है, जहां रेडॉक्स-सक्रिय लिगेंड को अपेक्षाकृत कम ओवरपोटेंशियल पर इलेक्ट्रोकैटेलिटिक डब्ल्यूओ प्रतिक्रियाओं की सहायता के लिए दिखाया गया था। इसलिए, रेडॉक्स-सक्रिय लिगेंड द्वारा समर्थित एलटीएम इलेक्ट्रोकेटेलिस्ट इलेक्ट्रोकैटेलिटिक डब्ल्यूओ प्रतिक्रियाओं के विकास के लिए एक आशाजनक रणनीति है। हमने कल्पना की कि एल्कोक्साइड दाता परमाणुओं वाले रेडॉक्स-सक्रिय और इलेक्ट्रॉन समृद्ध लिगेंड डब्ल्यूओ प्रतिक्रियाओं के लिए आवश्यक उच्च-वैलेंट धातु परिसरों तक आसान पहुंच को सक्षम कर सकते हैं।

अध्याय 1. परिचय

यह अध्याय आणविक 3 डी संक्रमण धातु परिसरों के इलेक्ट्रोकैटेलिटिक जल ऑक्सीकरण के संक्षिप्त अवलोकन का वर्णन करता है। अध्याय प्रतिक्रिया मध्यवर्ती के लक्षण वर्णन पर भी केंद्रित है जो साहित्य में अलग और विशेषता थी। इसके अलावा, परिचय अध्याय में उन वर्तमान चुनौतियों का वर्णन किया गया है जिन्हें अभी तक पानी के विभाजन प्रतिक्रियाओं के लिए कुशल उत्प्रेरक विकसित करने के लिए दूर नहीं किया गया है।

अध्याय 2. आणविक कॉपर कॉम्प्लेक्स की इलेक्ट्रोकैटेलिटिक जल ऑक्सीकरण गतिविधि: रेडॉक्स सक्रिय लिगेंड का प्रभाव

इस अध्याय में दो आणविक तांबा (II) परिसर दो रेडॉक्स-सक्रिय N2O2 दाता लिगैंड द्वारा समर्थित हैं जिन्हें विभिन्न स्पेक्ट्रोस्कोपिक तकनीकों के माध्यम से संश्लेषित और विशेषता दी गई है। दोनों परिसर कार्बोनेट में उत्प्रेरक जल ऑक्सीकरण प्रतिक्रिया दिखाते हैं और प्रयोगात्मक टिप्पणियों और सैद्धांतिक गणनाओं के आधार पर इलेक्ट्रोकैटेलिटिक डब्ल्यूओ प्रतिक्रिया के लिए संभावित प्रतिक्रिया तंत्र का प्रस्ताव करते हैं। अध्ययन आणविक तांबा परिसरों के इलेक्ट्रोकेमिकल पानी ऑक्सीकरण पर दाता लिगेंड के इलेक्ट्रॉन समृद्ध रेडॉक्स-सक्रिय एन 2 ओ 2 सेट की भूमिका को भी दर्शाता है।

अध्याय 3. कॉपर (III) कॉम्प्लेक्स के संरचनात्मक और स्पेक्ट्रोस्कोपिक लक्षण वर्णन और बाद में एक-इलेक्ट्रॉन ऑक्सीकरण प्रतिक्रिया और प्रतिक्रिया अध्ययन

इस अध्याय में, उच्च-वैलेंट तांबा परिसर के महत्व पर चर्चा की गई है। +II और +III ऑक्सीकरण अवस्थाओं में रेडॉक्स गैर-निर्दोष ओ-पीडीए पाड़ के आधार पर लिगैंड के टेट्राडेंट एन 2 ओ 2 दाता सेट के साथ समन्वित तांबा परिसरों के लक्षण वर्णन के बारे में विस्तार से अध्ययन। अध्ययन उच्च-वैलेंट लिगैंड-ऑक्सीकृत क्यू (III) परिसरों के विस्तृत लक्षण वर्णन का भी प्रतिनिधित्व करता है। कॉपर (III) प्रजातियों के

प्रतिक्रियाशीलता अध्ययन को कमजोर सी-एच / ओ-एच बॉन्ड वाले सब्सट्रेट्स की ओर खोजा जाता है, और प्रतिक्रिया तंत्र का प्रस्ताव दिया जाता है।

अध्याय 4 में। तटस्थ जलीय माध्यम पर आणविक तांबा परिसरों के इलेक्ट्रोकैटेलिटिक जल ऑक्सीकरण पर संरचनात्मक लचीलेपन का प्रभाव

इस अध्याय में, एन 4 दाता लिगैंड द्वारा समर्थित दो तांबा परिसरों को आगे डिजाइन और संश्लेषित किया गया है जो तटस्थ जलीय माध्यम पर इलेक्ट्रोकेटेलिस्ट के रूप में भी कार्य करते हैं और दिखाते हैं कि संरचनात्मक परिवर्तन पानी ऑक्सीकरण प्रतिक्रिया के प्रति उनकी प्रतिक्रिया को कैसे प्रतिबिंबित कर सकता है।

अध्याय 5. आणविक कोबाल्ट कॉम्प्लेक्स के जल ऑक्सीकरण प्रतिक्रिया में शामिल प्रतिक्रिया मध्यवर्ती का लक्षण वर्णन

यह अध्याय दो रेडॉक्स-सक्रिय एन 2 ओ 2 दाता लिगैंड बैकबोन द्वारा समर्थित दो कोबाल्ट परिसरों के संश्लेषण और लक्षण वर्णन से संबंधित है। दोनों परिसर फॉस्फेट बफर में इलेक्ट्रोकैटेलिटिक पानी ऑक्सीकरण दिखाते हैं। यह अध्ययन विभिन्न स्पेक्ट्रोस्कोपिक तकनीकों द्वारा पानी ऑक्सीकरण प्रतिक्रिया के दौरान शामिल दो प्रतिक्रिया मध्यवर्ती के लक्षण वर्णन पर भी ध्यान केंद्रित करता है जो डब्ल्यूओ प्रक्रिया में शामिल हैं।

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Abbreviations

Technical terms

CT:	charge transfer
deg.:	degree (^{0})
e^-:	electron
E:	total energy
J:	coupling constant
m/z:	mass per charge
$[M]^+$:	molecular ion peak
Q:	charge
RT:	Room temperature (293K)
S:	Electron spin
T:	tesla
TON:	Turnover number
TOF:	Turnover frequency
V:	voltage

Techniques

CV:	cyclic voltammetry
DFT:	density functional theory
EPR:	electron paramagnetic resonance
ESI:	electrospray ionisation
EXAFS:	extended x-ray absorption fine structure
GC:	gas chromatography
IR:	infrared spectroscopy
MS:	mass spectroscopy
NMR:	nuclear magnetic resonance
PPMS:	physical property measurement
UV-Vis:	ultraviolet-visible spectroscopy
XANES:	x-ray absorption near edge structure
XPS:	x-ray photoelectron spectroscopy
XRD:	x-ray diffraction

Units

A:	ampere
A^0:	angstrom (10^{-10}m)
C	coulomb
cal	calorie
^{0}C:	degree celsius
cm.:	centimetre
eV:	electron volt
F:	faraday
G:	gauss
h:	hour
K	Kelvin
Kcal:	kilocalorie
μA:	micro ampere
m:	meter
M:	molar
mA:	milliampere
min.:	minute
mm:	millimeter
mT:	millitesla
mV	millivolt
nm:	nanometer (10^{-9} m)
s:	second
T	tesla
V	volts
μ_B:	Bohr magneton

Latin expressions

et al:	and coworker
e.g.:	for example
i.e.:	namely
tert-:	tertiary
vs:	versus, against

Symbols

λ:	Wavelength (nm)
E:	electrode potential
Ɛ:	extinction coefficient ($M^{-1}cm^{-1}$)

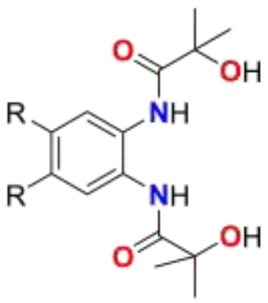
i:	current
ΔG:	Gibbs free energy
$\Delta H^{\ddagger}$:	activation enthalpy
k:	rate constant
$\Delta S^{\ddagger}$:	activation entropy
T:	temperature
μ_{eff}:	magnetic moment
η:	overpotential
ν:	scan rate

Solvents and reagents

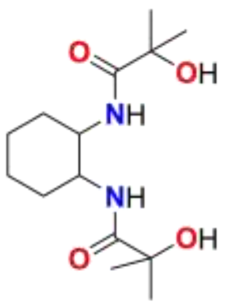
^{n}BuLi:	n-butyllithium
CH_2Cl_2:	dichloromethane
Et_2O:	diethylether
Et_3N:	triethylamine
HCl:	Hydrogen chloride
KBr:	Potassium bromide
MeCN:	acetonitrile
MeOH:	methanol
NMe_4OH:	tetramethylammonium hydroxide
THF:	tetrahydrofuran
TEMPOH:	1-hydroxy-2,2,6,6-tetramethyl-piperidine
BNAH:	1-benzyl-1,4-dihydronicotinamide
4-OMe-2,6-DTBP:	4-methoxy-2,6-ditertbutylphenol
2,6-DTBP:	2,6-ditertbutylphenol
o-PDA:	*ortho*-phenylenediamine
$SOCl_2$:	thionyl chloride

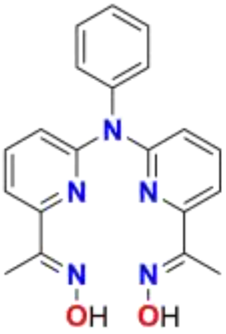
Ligands and Complexes Used

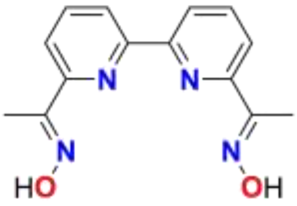
Ligands


R = H, H_4**L**$^{\mathbf{1}}$

R = CH$_3$, H_4**L**$^{\mathbf{2}}$


H_4**L**$^{\mathbf{3}}$


H_4**L**$^{\mathbf{4}}$


H_4**L**$^{\mathbf{5}}$

Complexes

$(NMe_4)_2[Cu^{II}(L^1)]$ (**1**)

$(NMe_4)_2[Cu^{II}(L^2)]$ (**2**)

$(NMe_4)[Cu^{III}(L^1)]$ (**3**)

$(NMe_4)[Cu^{III}(L^2)]$ (**4**)

$(NMe_4)_2[Cu^{II}(L^3)]$ (**5**)

$(NMe_4)[Cu^{III}(L^2)]$ (**6**)

$[Cu^{II}(HL^4)](ClO_4)$ (**7**)

$[Cu^{II}(H_2L^5)](ClO_4)_2$ (**8**)

$(NMe_4)[Co^{III}(L^1)]$ (**9**)

$(NMe_4)[Co^{III}(L^2)]$ (**10**)