Abstract

The coordination chemistry of iron and copper has a rich history. The diverse presence and catalytic role of these two metals in biosphere prompted inorganic chemists to synthesize a sea of coordination compounds in a vision to reproduce their natural counterparts. Discovery of tyrosyl radicals in the active sites ribonucleotide reductase (RNR) and galactose oxidase (GO) in last two decades stimulated synthesis of coordination compounds that contain metal coordinated phenolate and its one electron oxidized radical. These compounds obtained so far had striking similarities with their biological counterparts in electronic and magnetic properties. Hence for a better understanding these bio catalytic processes these compounds have gained importance over the last few years. In addition, the occurrence of polyiron and polycopper centers in ferritin, nitrous oxide reductase and particulate methane monooxygenase provided the main thrust for synthesis of polynuclear iron and copper complexes. The importance of these complexes lies in their interesting magnetic properties. The thesis entitled **"Studies on The Coordination Chemistry of Iron(III) and Copper(II) with Modified Salen and Amino Acid ligands"** is the result of our endeavor to develop phenoxide donor ligands for binding copper and iron to produce metal coordinated phenoxyl radical and generation of multinuclear iron and copper compounds.

The thesis has been divided into seven chapters. The contents of each chapter are described briefly.

Chapter-1: General Introduction

Chapter 1 of the thesis gives non exhaustive background information to the iron and copper chemistry, their biological importance and highlights the scope of work in the field. Then the aim and objective of the present work has been defined.

Chapter-2: Methods for Purification of Solvent and Starting Materials and Particulars of Equipments and Instruments Used

Methods used for the purification of solvents and starting materials, the relative particulars of instruments/equipment used for the characterization and structural assessment of the synthesized ligands and compounds are described in this chapter.

Chapter 3: Iron(III) Coordinated Phenoxyl Radicals from the Sterically Hindered Iron(III) Salen Complexes

This chapter deals with synthesis of three Salen ligands, viz.3,3′,5,5′-tetra-*tert*-butyl salen, 3,3′-di–*tert*-butyl 5,5′-di-methoxy salen and 3,3′,5,5′-tetra-bromo salen and their complexes with $FeCl_3$. One of the complexes has been structurally characterized. The electrochemical properties of the complexes have been determined and subsequently the complexes have been oxidized chemically with $(NH_4)Ce(NO_3)_6$ and the oxidized products have been identified to be Fe(III) coordinated phenoxyl radicals on the basis of UV-visible spectroscopy.

Chapter 4: A New Trinuclear Iron Complex of a Tridentate Modified Amino Acid Ligand with a $\{Fe_3(\mu_2\text{-}OMe)_3(\mu_3\text{-}OH)\}$ Core

In this chapter the synthesis and characterization of a ligand L^4H_2 {(3, 5-di *tert*-butyl-2-hydroxybenzyl)amino}acetic acid and its triiron(III) complex with a *"voided-cubane"* structure with $[M_3(\mu_3\text{-}OH)(\mu_2\text{-}OMe)]$ core has been described. The complex is weakly antiferromagnetic. Preliminary electrochemical results indicate a possible Fe(II)→Fe(III) oxidation in the cation and iron based reduction in the anion.

Chapter 5: A Double Helical Iron(III) Complex of an Optically Active Amino Acid Ligand

Synthesis of a new modified optically active amino acid ligand L-2-(3,5–di-*tert*-butyl-2-hydroxybenzylamino)-succinic acid (L^5H_3) derived from L-aspartic acid and its left handed double helical iron(III) complex constructed utilizing both hydrogen bonding interaction and coordination chemistry has been described in this chapter. The two iron (III) centers in the helix are magnetically non-interacting. Preliminary electrochemical results indicate possible generation of coordinated phenoxyl radicals and higher oxidation states of iron.

Chapter 6 Synthesis and Characterization of Two New Copper(II) Complexes Containing Tridentate Modified Amino Acid Ligands, [CuL(H_2O)(Pyz)], and their Oxidation to a Copper(III) Phenoxyl Radical Complex

Synthesis and characterization of two new copper complexes, [$CuL^4(H_2O)(Pyz)$] **(6)** and [$CuL^6(H_2O)(Pyz)$] (7) {L^4H_2= {(3,5-di-*tert*-butyl-2-hydroxybenzyl)amino}acetic acid; L^6H_2 = 2-(3,5-di-*tert*-butyl-2-hydroxybenzylamino)-3-methyl-butyric acid; Pyz = pyrazole} along with the synthesis and characterization of the new optically active tridentate ligand, 2-(3, 5-di-*tert*-butyl-2-hydroxybenzylamino)-3-methyl-butyric acid (L^6H_2), derived form L-valine has been described in this chapter. One of the complexes has been structurally characterized. These two mononuclear ternary copper(II) complexes have been oxidized chemically and electrochemically to generate corresponding copper(III) coordinated phenoxyl species. The radical species has been characterized by UV-visible spectroscopy and EPR spectroscopy.

Chapter 7: A New Bowl Shaped Trinuclear Copper(II) Complex - Synthesis, Structure and Magnetic Properties

In this chapter synthesis and characterization of a bowl shaped trinuclear complex $Na_3[\{(CuL^5(H_2O))_3Na(H_2O)(\mu_2\text{-}H_2O)Na\}\{(CuL^5(H_2O))_3Na(H_2O)\}].CH_3OH.\ 6H_2O$, (8) of a modified amino acid ligand L-2-(3,5-di-*tert*-butyl-2- hydroxy benzyl amino)-succinic acid has been described. However the magnetic interaction between the three Cu(II) centers through O-Na-O bridges in the complex is very weak and antiferromagnetic. Preliminary electrochemical results indicate a possible Cu(II)→Cu(III) oxidation and phenoxide to phenoxyl radical oxidation in the complex.