

Synthesis, Characterization Spectrafluorometric Studies and Catalytic Activity of Water Soluble Cysteine Cu (II) and Ni (II) Metal Complexes

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Abstract: The Complexes of Cu (II) and Ni (II) with amino acid cysteine were synthesized and characterized by FT-IR and spectrafluorometric Studies. The FT-IR spectra shows some new band which confirms that the complex is formed. The spectrafluorometric study of amino acid metal complexes shows that excitation wave length decrease with decrease in the polarity of medium. The amino acid nickel (II) complex exhibits a strong fluorescence emission at 340 nm in DMF medium. This may be tentatively assigned to the ligand to metal charge transfer (LMCT). In these complexes the amino acid coordinated to 1:2 with metal and they exhibits octahedral geometry. The catalytic activities of these complexes were studied in olefins using eco-friendly nontoxic molecular oxygen as oxidant.

Keywords: Amino acid, Metal Complexes, Cysteine, Spectrafluorometric, Molecular Oxygen.

1 Introduction

Amino acids are a group of biomolecules that contains nitrogen bearing amine group, and a carboxylic acid group. The general formula of amino acids is $H_2NCHRCOOH$, where R is an organic substituent. The amino group in amino acid under goes various chemical modifications at physiological pH value. The most important modification is Schiff base modification.

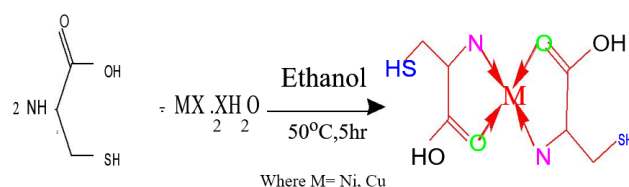
The reactions that occur between oxygen and organic compounds have a major role in living organisms, because the produced energy is used to power all biochemical systems. Catalysis is the most important process that accelerates the rate of reaction for such reaction which occurs very slowly.

The addition of oxygen to alkenes is one of the important reactions in industrial chemistry. The epoxy compounds can react with functional groups like amines, phenols and others containing active oxygen and act as intermediate compounds in the synthesis of pesticides, pharmaceutical and perfumery products, polyethers and so on. There are some reports of metal complexes that are used as catalysts in the epoxidation reaction. The Mo complexes are known to be efficient catalysts in the epoxidation of alkenes with organic hydroperoxides. The use of other transition metal ions in the form of homogeneous or heterogeneous catalysts has also been described [1, 2].

Polymer coated Cu(II) complexes with L-phenylalanine and

L-valine were obtained and used as catalysts for the epoxidation of alkenes with m-chloroperbenzoic acid. The selectivity for the obtained epoxide was 92% - 94% [3]. Polymer-anchored amino acid ruthenium com-plexes were used as epoxidation catalysts. The polymer carrier was Merrifield resin with valine attached to it and treated with ruthenium (III) chloride. Neither selective epoxidation with nor bornylene and cyclooctene was observed while for styrene, benzaldehyde and acetophenone were obtained besides epoxy [4]. Efficient epoxidation catalysts were obtained based on tungsten oxide [5] and molybdenum tricarbonyl [6]. New catalysts were also obtained through the treatment of MCM-41 molecular sieve with 3-aminopropyl-trimethoxysilane and acetylacetone [7].

2 Experimental



Scheme 1

Amino acid Cysteine 5gm were treated with 2.5gm of transition metal in presence of ethanol at temperature 500C at 24 hr. greenish and a light yellow color indicates the formation of copper and nickel amino acid complex is formed. The power crystals were cooled filtered a then

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dried. Yield 1.2gm.

2.1 FT-IR Spectrum of Cystein and its Complexes

The vibrational for cystein modes due to carboxylate and amino groups was found to exist at 1680-1540 cm^{-1} (COO^-), 3150-3000 cm^{-1} ($-\text{NH}_2$). Further to this 1410 cm^{-1} (weak) for symmetric stretching of COO^- and 660 cm^{-1} for COO^- (deformation). The peak at 1660-1610 cm^{-1} and 1550-1480 cm^{-1} were also assigned for ($-\text{NH}_2$) vibrations for bending. Changes were observed in the IR bands of ($-\text{NH}_2$) and (COO^-). The new bands were exhibited in the range of 400-660 cm^{-1} , which are tentatively assigned for the M-N coordination and M-O coordination was observed in the range of 940-1210 cm^{-1} [8], [9]. Thus we can say that the metal complexes shifts in M-C=O and M-NH₂ bands as well as the widening of the bands were clearly reveals the formation of metal complexes with a bi dentate mode [10][11]. Fig 1. IR spectrums of complexes

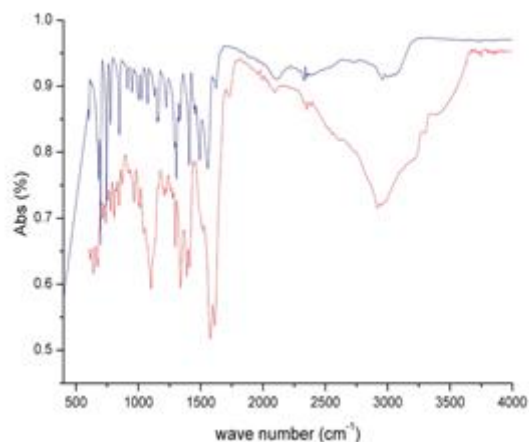


Fig. 1 FTIR Complex of Cysteine Cu (II) and Ni (II) Complexes.

2.2 Fluorescence study

The incorporation of Metal in to the amino acid may lead to significant changes in fluorescence properties of ligand. The properties including increase of intensity shift of wavelength and quenching of the fluorescence. The fluorescence spectra of amino acid Cu (II) and the Amino acid Ni (II) shows various changes in emission of wavelength with the variation of solvent. The amino acid copper (II) shows excitation wavelength at 350 nm at room temperature in DMF medium. The excitation wavelength decrease with decrease in the polarity of medium. The amino acid nickel (II) complex exhibits a strong fluorescence emission at 340 nm in DMF medium. This may be tentatively assigned to the ligand to metal charge transfer (LMCT) Fig. 2 and 3.

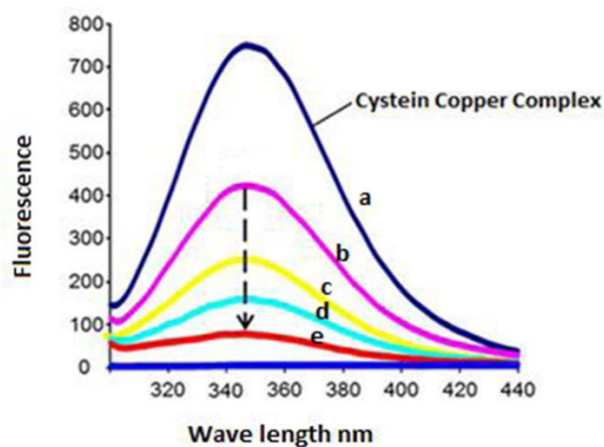


Fig. 2 shows the florescence diagram of Cu (II) cysteine. Where a, b, c, d, e are the DMF, DMSO, CCl_4 , Benzene, water solvent medium respectively

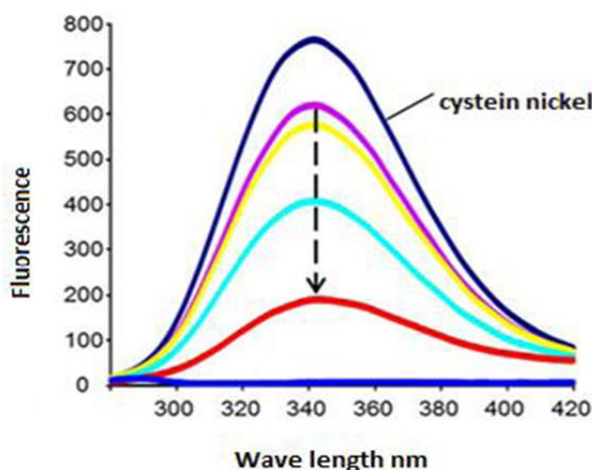
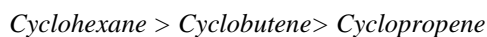


Fig.3 Shows the florescence diagram of cysteine Ni (II) complexes.

2.3 Catalytic Oxidation Reactions

Required amount of catalyst is dissolved into the required amount of solvent and then in other Beaker required amount of polymer is dissolved into the particular solvent. Both the solutions were mixed and stirred at particular time and temperature. The progress of reaction is checked by using thin layer chromatography. After the complexation of reaction, the Spectra chemical techniques are using that show the formation of catalyst takes place. The catalyst is used for the Oxidations reaction particularly in the oxidation of olefins [12],[13][14]. The optimum temperature for carrying out the oxidation is 25°C in presence of methanol as solvent and 70mg of catalyst. The rate of oxidation of various olefins follows the order [15]



3 Conclusions

Three complexes of Cu (II), Ni (II) with amino acid cysteine were prepared by refluxing the amino acid and metals. The complexes were characterized by elemental analysis, FT-IR spectrum. The Spectrafluorometric Studies shows the new wavelength at 340 nm of nickel amino acid complex which is due to LMCT. In these complexes the amino acid coordinated 1:2 ratios with metals and they exhibited different geometries. All the complexes were found to be active for the oxidation of some olefins substrates under mild conditions of temperature and pressure using molecular oxygen as the oxidant. The influence of concentration of the catalyst and the substrate on the rate of reaction has been carried out. In the case of cyclohexane as the substrate, the formation of cyclohexanol as the oxidation product was confirmed by GC – MS technique.

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