RESEARCH ARTICLE Am. J. PharmTech Res. 2016; 6(4) ISSN: 2249-3387

AMERICAN JOURNAL OF PHARMTECH RESEARCH

Journal home page: http://www.ajptr.com/

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

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ABSTRACT

The Complexes of Co (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 water 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

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Received 14 June 2016, Accepted 19 June 2016

Please cite this article as: Parrey IR *et al.*,Synthesis, Characterization Spectrafluorometric Studies and Catalytic Activity of Water Soluble Cysteine Co (II) and Ni (II) Metal complexes .American Journal of PharmTech Research 2016.

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.

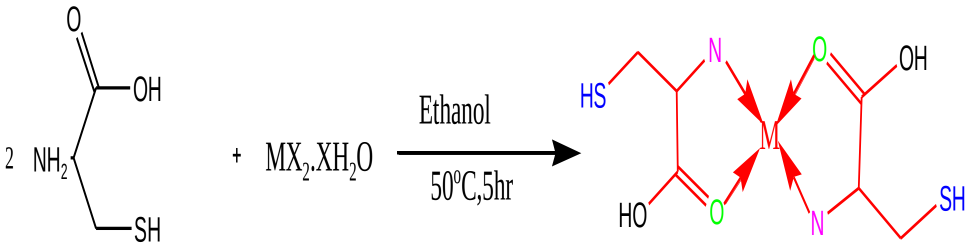
The addition of oxygen to alkenes is one of the important reactions in industrial chemistry. The epoxy compounds can react with functional groups like amines, phenols and others containing active oxygen and act as intermediate compounds in the synthesis of pesticides, pharmaceutical and perfumery products, poly ethers 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].

The Polymer metal complexes of 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 complexes were used as epoxidation catalysts. The polymer carrier was Merrifield resin with valine attached to it and treated with ruthenium (III) chloride. Selective epoxidation with norbornylene and cyclooctene was observed while for styrene, benzaldehyde and acetophenone were obtained besides epoxy [4]. Efficient epoxidation catalysts were obtained on the basis of tungsten oxide [5] and molybdenum tri carbonyl [6].

MATERIALS AND METHOD

Synthesis of amino acid metal complex:

Amino acid Cysteine 5gm were treated with 2.5gm of transition metal in presence of ethanol at temperature 50^0C at 24 hr. greenish and a light yellow color indicates the formation of cobalt and nickel amino acid complex is formed. The power crystals were cooled filtered a then dried. Yield 1.2gm



Where M= Ni, Co

New catalysts were also obtained through the treatment of MCM-41 molecular sieve with 3-aminopropyl-trimethoxysilane and acetyl acetone [7].

RESULTS AND DISCUSSION

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} (–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 (–NH$_2$) vibrations for bending. Changes were observed in the IR bands of (–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 also 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–NH$_2$ bands as well as the widening of the bands were clearly reveals the formation of metal complexes with a bi dentate mode [10,11] Figure 1a is the respective IR spectrums of complexes

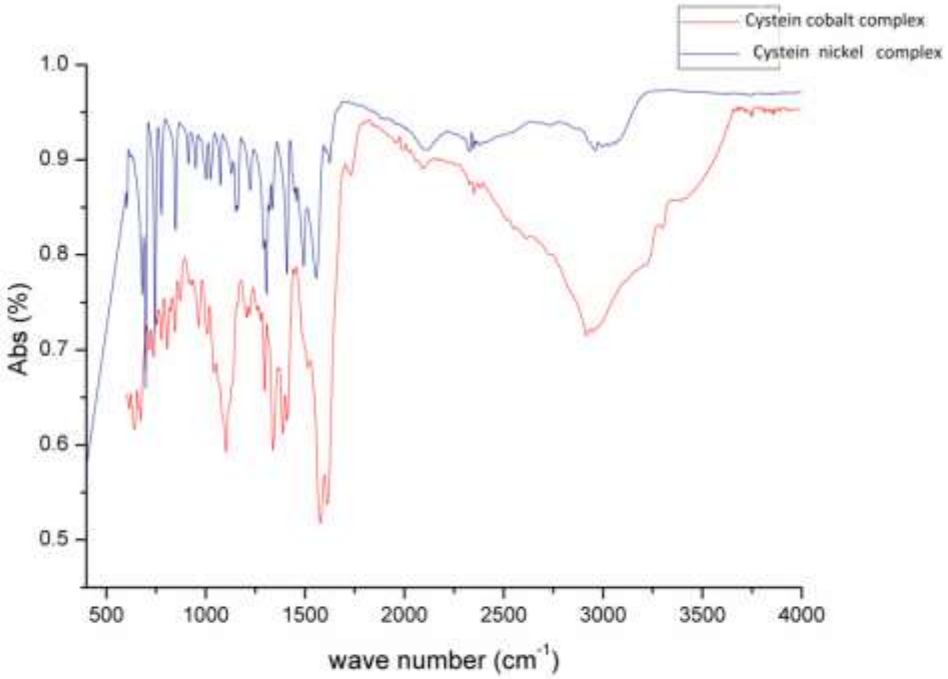


Figure1a: FT-IR Spectrum of cystein cobalt and cystein nickel metal complexes

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 wave length and quenching of the fluorescence. The fluorescence spectra of amino acid Co (II) and the Amino acid Ni (II) shows various changes in emission of wavelength with the variation of solvent. The amino acid cobalt (II) shows excitation wave length at 350nm at room temperature in Water medium. The 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 water medium. This may be tentatively assigned to the ligand to metal charge transfer (LMCT)

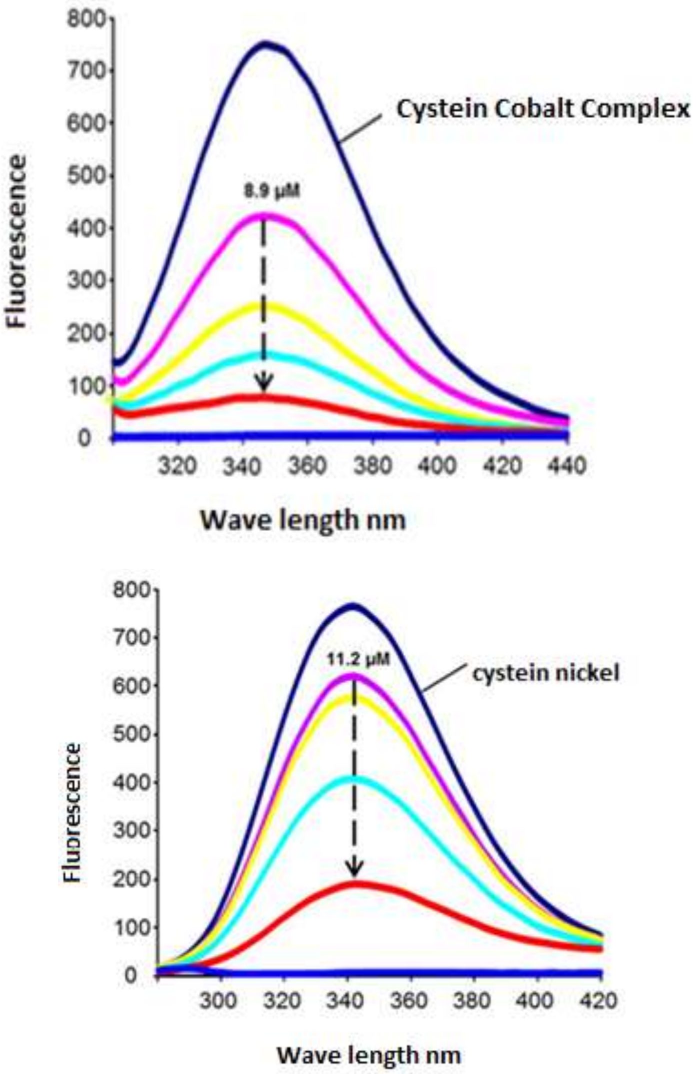


Figure 2shows the fluorescence diagram of (A) cysteine Co (II) and (B) Ni (II) at various solvent concentrations

Catalytic Oxidation Reactions

Required amount of catalyst is dissolved into the required amount of solvent and then in otherBeaker required amount of polymer is dissolved into the particular solvent. Both the solutionswere 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 [12-14]the optimum temperature for carrying out the oxidation is 25^0C in presence of methanol as solvent and 70mg of catalyst. The rate of oxidation of various olefins fallows the order [15,16]

Cyclohexane >Cyclobutene>Cyclopropene

CONCLUSION

Two complexes of Co (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 Studiesshows 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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