

Synthesis, characterization and catalytic activity of Schiff base Cu (II) metal complex

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ABSTRACT

This study reports the synthesis of chitosan anchored Schiff base, [(2-oxo-1H-indol-3-ylidene) amino] chitosan and its Cu (II) metal complex. The complex was characterized by elemental analysis, FT-IR Spectrum, Thermogravimetry analysis. The crystallinity of the compound was analyzed by X-ray diffraction technique. The catalytic efficiency of complex was studied in the oxidation of alcohols namely propanol, n-butanol, n-hexanol and benzyl alcohol using eco-friendly and easily available molecular oxygen as an oxidant. Furthermore the effects of various parameters including temperature, catalyst amount and effect of solvent have also been studied. The complex was found a suitable source in bringing out the oxidation reactions.

Keywords: Chitosan, Schiff base, Catalytic activity, Oxidation, Non-toxic, Molecular oxygen.

1. Introduction

Chitosan is a naturally occurring linear polysaccharide, closely related to chitin both are naturally abundant and renewable polymers. Chitosan and chitin show excellent properties like biodegradability, biocompatibility, non-toxicity and adsorption [1]. The polymer is widely distributed in the animal kingdom. Chitin can be extracted from crustacean shells, insects, fungi, and other biological materials [2,3].

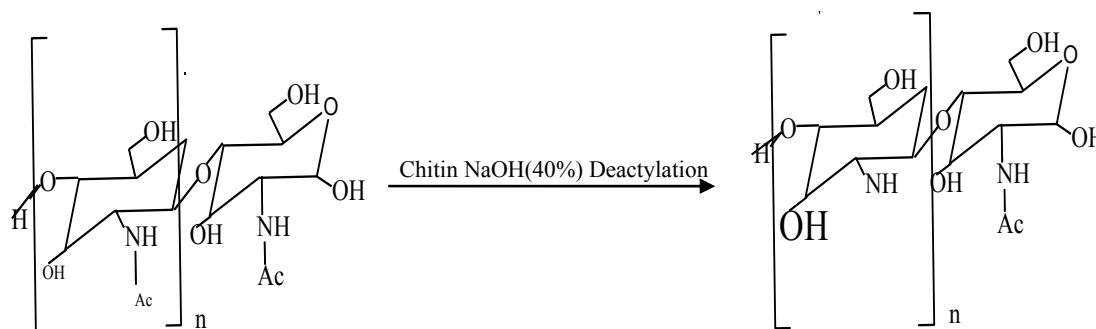
Chitosan is a copolymer whose chemical structure and its extraction from chitin are shown in Scheme 1. The numbers on the extreme left ring are conventionally assigned to the six carbons in the glycopyranose ring from the C-1 to C-6. Substitution at C-2 may be an acetamido group. Chitosan contains more than 50% acetamido residues on the C-2 of the structural unit while amino groups predominate. In chitin the degree of deacetylation (DD) serves as a diagnostic character which classifies the biopolymer as chitin or chitosan [4]. The free amino group available in the chitosan structure enables it to undergo variety of chemical modifications and substitution processes. It is because the reactions of chitosan are considerably more versatile than cellulose [5,6].

The reaction of this free amino group with the aldehydes and ketones are resulting in the formation of Schiff base. The ligands (Schiff bases) are often reported for the reason that they offer opportunities for inducing biological activity [Schiff], adsorption of metallic ions and the support of metal complex catalysts [7,8]. Schiff base modified chitosan complexes have been the most widely studied coordination compounds in the past few years, since they are becoming increasingly important as biochemical, antimicrobial and catalytic reagents [9-12].

The catalytic reaction of organic compounds especially the functionalization of alcohols via the oxidation reactions using molecular oxygen as oxidant is the very useful reaction. Research on the functionalization of alcohols via oxidation reactions requires special attention due to immense industrial importance of functionalized products. Some reports have been found for the oxidation of benzyl alcohol under aerobic room temperature condition using different transition metal complexes as catalysts [13].

The present work reports on the synthesis of modified chitosan based Schiff base ligand metal complex and its applications in the oxidation of alcohols in presence of ecofriendly nontoxic nature molecular oxygen as oxidant.

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Scheme 1. Extraction of chitosan from chitin.

The catalyst is active towards the oxidation of alcohols. Further the effect of various parameters like temperature, catalyst amount, effect of solvent was also reported.

1.1. Materials and Instruments

Medium molecular weight chitosan powder was obtained from Hi-media chemical company India. This chitosan powder was further purified by the dissolution of 2.5 g chitosan powder in 1 liter of 0.5 molL⁻¹ acetic acid solution. Isatin was purchased from Merck-India. All other chemicals and solvents were obtained from Merck and used as received. All chemical reactions were carried under aerobic conditions. The percentages of carbon, hydrogen and nitrogen contents were analyzed using Carlo Erba 1108 model elemental analyzer. FT-IR Spectra of polymer supported metal-complex at various stages of synthesis was recorded using Perkin Elmer spectrometer. Mass Spectrum was recorded using model Q-TOF micro mass ESI-MS source Thermo gravimetric analysis was recorded using EXSTAR 6000 whose temperature ranges from 50°C to 800°C in a nitrogen atmosphere with Alumina as reference standard. Powder X-ray diffraction was accomplished using an x-ray diffractometer (XPRT PRO PANalytical, National Physical Laboratory New Delhi) for phase identification. The patterns were run with Cu K- α radiation with a secondary monochromator ($\lambda=0.1545\text{nm}$) at 40kV and 30mA. The analyses of various liquid products obtained in the catalytic oxidation reactions were carried out by Hewlett-Packard gas chromatography (HP 6890) having FID detector, a capillary column (HP-5), with a programmed oven temperature from 50 to 200°C and a 0.5 cm³ min⁻¹ low rate of N₂ as a carrier gas.

2. Experimental

2.1. Synthesis of Schiff base modified chitosan

Chitosan (1 g, 5 mmol) was dissolved in the dilute acetic acid (2%) in presence of base and then stirred for 4 h at 20°C temperature. It was then add to

methanol solution of isatin (5 mmol) in a single necked flask and Stirred continuously in 15h at temperature 25°C. The resultant red brownish suspension was filtered and was thoroughly washed with methanol and then ether. The purified product was dried under vacuum at 50°C in 1h. washed with methanol and then ether. The purified product was dried under vacuum at 50°C in 1h.

2.2. Synthesis of Schiff base modified chitosan Cu complex

5 mmol of Schiff base modified chitosan was added to 5 mmol of CuCl₂·2H₂O in a flask the whole solution was magnetically stirred for 10 h at 70°C. The resultant green complex was washed with methanol and then dried under vacuum for 30 min. (Scheme 2).

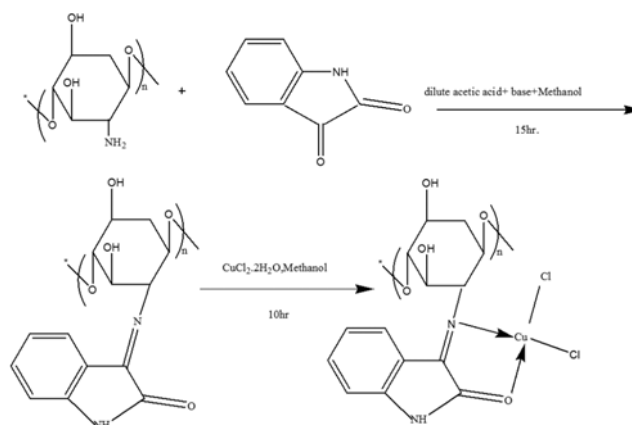
2.3. Catalytic Oxidation Reactions

To evaluate the catalytic activity of the Schiff base modified chitosan Cu catalyst, the oxidation of propanol, n-butanol, n-hexanol and benzyl alcohol was conducted using molecular oxygen as oxidant. The oxidation was studied by varying the reaction conditions. This includes the type of solvent, the temperature (30-90°C) reaction time and the amount of catalyst (90-180 mg). The Procedure of oxidation reaction was described in [14]. In the first step the catalyst was allowed to swell in the solvent for 15min. in round bottom flask to this was added 5mmol of propanol followed by 1 atm. O₂. The reaction mixture was stirred at desired temperature. At the end of specific time the contents were analyzed by gas chromatography. The peak position of the products was matched with the retention time of authentic sample. A control experiment in the absence of catalyst was also conducted. Similarly for other substrates same reaction conditions are used.

3. Results and discussion

3.1. Elemental analysis

The elemental analysis of the chitosan modified Schiff base ligand metal complex was shown in Table 1.



Scheme 2. Scheme for the synthesis of Schiff base modified Chitosan copper complex.

3.2. FT-IR spectra of chitosan modified Schiff base metal complex

FT-IR Spectrum of chitosan modified Schiff Cu ligand complex shows following important peaks (Fig. 1). A strong band at 3200 cm^{-1} analogous to the O-H stretching of chitosan. In the FT-IR spectrum of the Schiff base ligand a new band is observed at 1620 cm^{-1} due to C=N stretch of the newly formed azomethine group, another new band appears around 1490 cm^{-1} because of aromatic C=C stretch this band confirms that the Isatin has been successfully grafted on to the chitosan backbone [15]. The C=O stretching of amide group occurs at 1700 cm^{-1} . The formation of M-N and M-O occurs at $\sim 490\text{ cm}^{-1}$ and $\sim 420\text{ cm}^{-1}$ respectively [16, 17].

The C-O-C stretching band of chitosan occurs around 1000 cm^{-1} and β (1-4 glycoside) bridge band around 890 cm^{-1} - 1150 cm^{-1} were also found in FT-IR spectra of the complex which means that the metal complex has formed.

3.3. Electro-Spray Ionization Mass Spectra (ESI-MS) analysis

The proposed structure of polymer ligand Cu complex shows the peak at m/z 422.3 which corresponds to the moiety ($M-3\text{H}_2\text{O}$) of atomic mass m/z 424.1. Data obtained suggested that doing the reaction of chitosan with isatin there is loss one water molecule and in the

second step after the addition of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ Two water molecules removes. The base peak at m/z 232 corresponding to the loss of moiety ($M-\text{C}_6\text{H}_{11}\text{NO}_4\text{Cl}$) of atomic mass m/z 232 which suggested the removal of chitosan and one chlorine fragment from ligand Cu-complex. Another peak at m/z at 167.0 corresponding to the loss of moiety ($M-\text{C}_6\text{H}_{11}\text{NO}_4\text{CuCl}$) of m/z 161.1 from Schiff base modified Cu complex shown in Fig. 2.

3.4. Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis of chitosan ligand Cu complex shows three important different mass loss stages. The first mass loss of chitosan ligand metal complex occurs at ($\sim 6\%$) below 100°C which is due to the loss of physically adsorbed water molecules.

The second mass loss stage occurs at ($\sim 50\%$) $400\text{--}640^\circ\text{C}$ with the maximum endothermic decomposition peak which is due to the decomposition of free chitosan unit third stage at ($\sim 10\%$) at 650°C occurs due to the deformation of coordination bond between azomethine nitrogen and Cu ion and also decomposition of condensed chitosan unit. Similar mass loss stage has been reported with free chitosan and chitosan modified Schiff base [18]. The thermal stability of chitosan modified Schiff base shows lower thermal stability than free chitosan which is due to the decrease of the number of primary amine groups in Schiff base modification Fig. 3.

Table 1. Elemental analysis of Schiff base metal complex.

Compound	Molecular Formula	Mol. (wt.)	Yield (%)	Elemental Analysis (%)			
				Calculated (Found)			
				C	H	N	Cu
Modified chitosan	$\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_5$	290	67	57.93 (57.00)	4.86 (4.66)	9.65 (9.22)	-
Modified chitosan Cu Complex	$\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_5\text{Cu}$	424	62	39.59 (39.00)	3.32 (3.15)	6.60 (6.51)	14.96 (14.51)

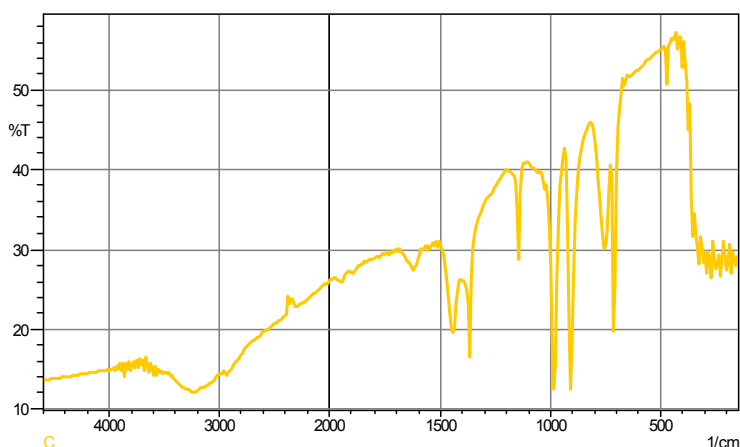


Fig. 1. FT-IR spectra of Schiff base metal complex

3.5. X-ray diffraction (XRD) spectroscopy

Due to the strong hydrogen bonding in chitosan it is outstanding crystalline biopolymer among all carbohydrate polymers [19]. The XRD patterns of Schiff base modified chitosan shows most significant peak at $\sim 2\theta=20^\circ$. The decrease in the Crystallinity of Schiff base modified chitosan is due to the deformation of hydrogen bonds in the chitosan after its structural modifications [20] Fig. 4.

3.6. X-ray diffraction (XRD) spectroscopy

The oxidation reaction of propanol was conducted using a chitosan modified Schiff base Cu metal complex. The results are shown in Table 2. The benzyl alcohol gives higher oxidation yield than propanol, n-butanol, and n-hexanol.

3.7. Effect of temperature

The reaction temperature has a strong influence on the progress of the benzyl alcohol oxidation. The effect of reaction temperature on the progress of oxidation of benzyl alcohol was studied at different temperatures in presence of catalyst. The oxidation reaction was carried out using 5 mmol of benzyl alcohol at 1atm.pressure in presence of methanol and toluene as solvent (1:1) for 3 h with different reaction temperatures from 30°C to 90°C, and results are shown in Table 3. Benzyl alcohol conversion was increased with increasing reaction temperature, although small conversion was detected when the reaction temperature was below 30°C. However, high temperature led to a quick decomposition of molecular oxygen, conversely lowering down the conversion. The optimum temperature was 70°C.

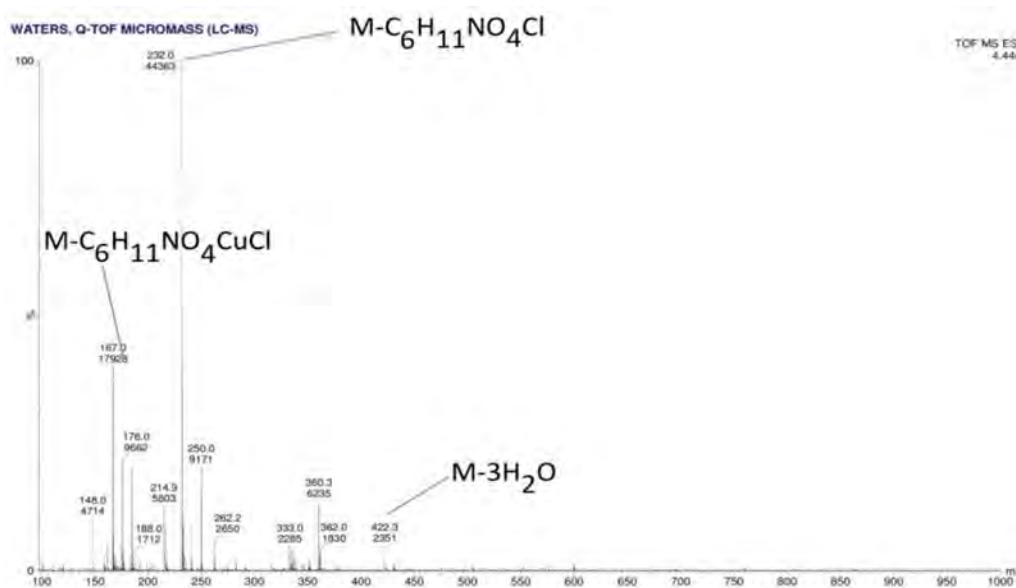


Fig. 2. ESI-MS analysis of Schiff base metal Complex.

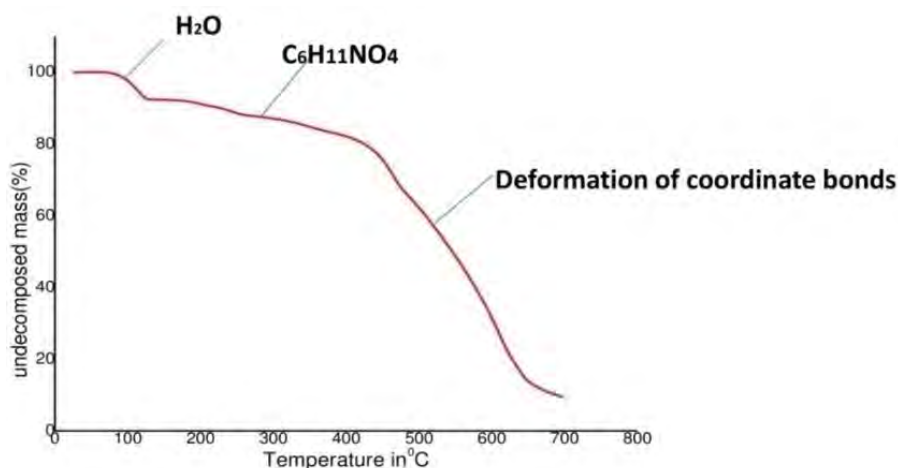


Fig. 3. Thermo-gravimetric analysis (TGA) of Schiff base metal complex. 6% mass loss at 1st stage. Below 100°C, 2nd loss 50% at 400-640 °C, 3rd loss 10% at 650°C. Crystalline index= 20%.

3.8. Effect of Catalyst

The effect of amount of catalyst on the oxidation of benzyl alcohol as a function of time is illustrated in Table 4.

A control experiment was also carried out with benzyl alcohol in the presence of molecular oxygen and without the addition of catalyst. It was observed that in the absence of any added catalyst, very poor conversion of benzyl alcohol was obtained. At low catalyst below 90 mg moderate conversion of benzyl alcohol was obtained. With the increase in catalyst amount from 90 mg to 150 mg, the conversion of benzyl alcohol increased. This may be due to the availability of more active sites of the catalyst that favors the accessibility of larger number of molecules of substrates and oxidant to the catalyst. Benzyl alcohol conversion remained almost constant upon further increase in catalyst amount to 180 mg, the optimum reaction conditions for the oxidation of

benzyl alcohol were as follows: benzyl alcohol (5 mmol), 1 atm. molecular oxygen, catalyst (150 mg), methanol: toluene (1:1) time (3 h) and temperature (70°C).

3.9. Effect of Solvent

In order to study the effect of solvents, several solvents were employed in the oxidation reaction of benzyl alcohol (5 mmol) with molecular oxygen (1 atm.) at 70°C keeping other parameters constant. The oxidation reaction was carried out in several polar and non-polar solvents.

The selected solvent should possess certain criteria such as it should be stable and it should dissolve the substrate and oxidant quantitative yields were observed with polar solvents such as water, acetonitrile (ACN), methanol and dichloromethane (DCM). The efficiency of the catalysts for oxidation of benzyl alcohol is higher in methanol and toluene medium.

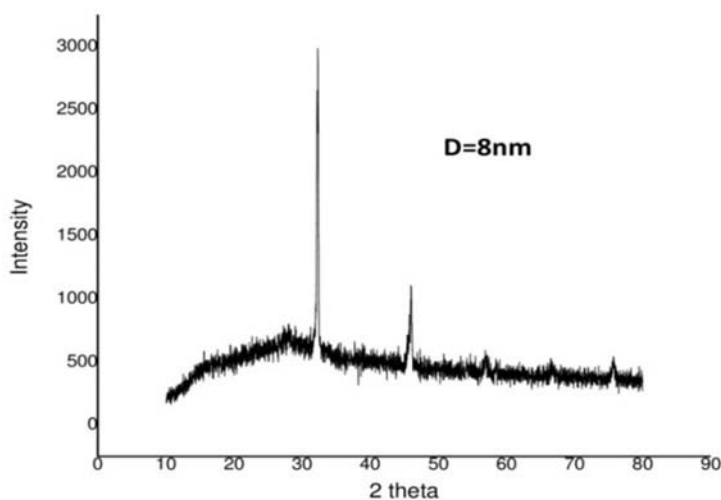


Fig. 4. Power XRD of Schiff base metal complex.

Table 2. Oxidation of Different alcoholic substrates.

Time (h)	Substrate	Product	Yield (%)	Selectivity (%)
3	Propanol	Propanone	52	61
3	Butanol	Butanal	44	52
3	Benzylalcohol	Benzaldehyde	58	66
3	Hexanol	Hexanone	37	55

Table 3. Effect of temperature.

Catalyst (mg)	Temp. (°C)	Time (h)	Yield (%)
150	30	3	52
150	50	3	48
150	70	3	58
150	90	3	45

4. Conclusions

Chitosan modified Schiff base complex of copper were synthesized. FT-IR spectra confirms the formation Schiff base metal complex. Thermal stability of Schiff base modified chitosan was found less than that of chitosan. Powder XRD shows the formation of a characteristic peak ($\sim 2\theta=20^\circ$) in Schiff base copper complex. Chemical modification of chitosan leads to increase in the roughness of the surface like metallation of modified chitosan Schiff base ligand results in the increase in the surface area and thus makes it good catalyst. The complex successfully catalyzed the oxidation of n- propanol, n-butanol, n-hexanol and benzyl alcohol into their oxidizing products. The main advantages of the present catalyst are ready accessibility, high product yield, robustness, high thermal stability and applicability for a variety of substrates. These catalysts are reused several times without appreciable decrease in their initial activities.

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Table 4. Effect of catalyst amount.

Catalyst (mg)	Temp. (°C)	Time (h)	Yield (%)
90	70	3	51
120	70	3	48
150	70	3	58
180	70	3	42

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