SYNTHESIS AND CHARACTERIZATION OF SCHIFF BASE METAL COMPLEX OF COBALT DERIVED FROM CHITOSAN AND BENZALDEHYDE.

BY

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PSC1808641

A PROJECT WRITTEN IN THE DEPARTMENT OF CHEMISTRY AND SUBMITTED TO THE FACULTY OF PHYSICAL SCIENCES IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF DEGREE OF B.SC CHEMISTRY OF THE UNIVERSITY OF BENIN, BENIN CITY. EDO STATE, NIGERIA

JULY, 2021

CERTIFICATION

We the designated certify that this project work was carried out and presented by **EZELIBE OLUOMA CELINE** in partial fulfillment of the requirement for the award of Bachelor of science degree (B.Sc.) Chemistry, in the Department of Chemistry, University of Benin, Benin City, Edo State.

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DEDICATION

I dedicate this project work to God Almighty for his infinite favors, strength and grace to pull through and to my parents **Mr and Mrs ERNEST EZELIBE** for their support prayers and assistance.

ACKNOWLEDGEMENT

My greatest gratitude goes to God Almighty for his unending blessings upon me and for the successful completion of this report.

I express my profound gratitude to all professors, lecturers and staff in the Department of Chemistry, Particularly I express my gratitude to my supervisor, Prof Arthur Jideonwu, who made this project work a success through his encouragement, patience, teachings and support.

To my lovely and ever supportive parents Mr. and Mrs. Ernest Ezelibe and also to my lovely siblings whose prayers and support went a long way in the success of this project work and during my course of study in the University of Benin, I sincerely appreciate you all.

My appreciation also goes to every persons that have contributed in one way or other to the success of this work, Most importantly to my friends turned sisters, Miss Love Okafor and Miss Precious Julius-Ndieze, I deeply appreciate them for never giving up on each other inspite all odds

TABLE OF CONTENT

1.0 INTRODUCTION.....,...................

ABSTRACT

Schiff bases and their complexes are versatile compounds synthesized from the condensation of an amino compound with carbonyl compounds and widely used for industrial purposes and also exhibit a broad range of biological activities including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties. Many Schiff base complexes show excellent catalytic activity in various reactions and in the presence of moisture. Over the past few years, there have been many reports on their applications in homogeneous and heterogeneous catalysis. The high thermal and moisture stabilities of many Schiff base complexes were useful attributes for their application as catalysts in reactions involving at high temperatures. The activity is usually increased by complexation therefore to understand the properties of both ligands and metal can lead to the synthesis of highly active compounds. The influence of certain metals on the biological activity of these compounds and their intrinsic chemical interest as multidentate ligands has prompted a considerable increase in the study of their coordination behaviour. Development of a new chemotherapeutic Schiff bases and their metal complexes is now attracting the attention of medicinal chemists.

CHAPTER 1

1.0 INTRODUCTION AND LITERATURE REVIEW

1.1. INTRODUCTION

1.1.1. BACKGROUND STUDY.

Hugo Schiff, a German scientist, is credited with being the first to characterize the byproducts of the reaction of primary amines with carbonyl compounds in 1864, giving rise to the compound "Schiff's base." In the study of coordination chemistry, the Schiff base and related metal complexes are particularly significant. With a double bond connecting the carbon and nitrogen atoms, Schiff bases are a large class of chemical compounds. Their versatility comes from the many ways they can be combined with different alkyl or aryl substituents. This kind of compound can be created in a lab or in nature. For many chemists and biochemists, Schiff bases have served as a major source of inspiration for many years. Schiff base compounds (-CH=N-) are drawing attention because of their adaptable metal binding mode. They are typically created by condensation of primary amines with chelating ligands that have N, S, and O as donor atoms. Due to their tiny size, high charge densities, and unoccupied (n-1) d orbital, transition metals have a great propensity to form coordination complexes. In the inorganic and bio-inorganic fields, which are related to some biological systems, the synthesis and application of Schiff bases and their coordination compounds have received considerable attention.

1.1.2. STATEMENT OF THE PROBLEM

Despite advances in surgical and medical procedures, infections and germs continue to be the leading causes of morbidity and mortality. The quest for novel compounds with antibacterial properties is necessary due to the growing microorganism resistance to existing antibacterial treatments having consequences on pathogenic organisms. To tackle the issue of resistance, which is being gradually developed by microorganisms, novel antibacterial agents must be continuously developed.

1.1.3. JUSTIFICATION

Since it has been discovered that the physio-chemical and biological activities of organic compounds are related to their structure, the study of Schiff bases' structure activity relationship (SAR), which establishes a link between chemical structure and biological activity, is anticipated to provide information on how to use Schiff bases as antibacterial agents in the future. Additionally, prior research demonstrated that Schiff base metal complexes are more potent than uncoordinated Schiff base (Atmaram and Kiran, 2011). Therefore, it is anticipated that new Schiff base metal complex appropriate as active components in antiseptics formulation would be found. This study was therefore necessary.

1.1.4.SIGNIFICANCE OF THE STUDY

The government, private businesses, and chemistry researchers will all benefit greatly from this study on the synthesis and characterisation of chitosan Schiff base and its metal complex. This study is expected to demonstrate the relevance of chitosan Schiff base in escalating microbial resistance to existing antibacterial agents. This research is required in the search for new compounds with potential effects against pathogenic organisms. This might inspire researchers to investigate other Schiff bases and their various metal complexes more thoroughly

1.1.5. SCOPE OF THE STUDY

This study focuses on the synthesis and characterization of chitosan Schiff base and it's cobalt metal complex.

1.1.6. AIM/ OBJECTIVE

The aim of this research work is to synthesize and characterize a Schiff base and it's cobalt metal complex from an amine and aldehyde.Therefore the specific objectives of the study include the following:

- To synthesize chitosan
- To synthesize chitosan Schiff base
- .To characterize the Schiff base metal complex

1.2. LITERATURE REVIEW

1.2.1.SCHIFF BASES

A Schiff base is a class of chemical compounds with a functional group made up of a carbon-nitrogen double bond, where the nitrogen atom is attached to an aryl or alkyl group (R) but not to hydrogen. Azomethine is the same as the Schiff base. Hugo Schiff is honored by the names of these substances. Through the imine nitrogen and another group, typically connected to the aldehyde, this type of ligands can coordinate metal ions. Schiff bases are still created by chemists, and today's 'privileged ligands' are active, well-designed Schiff base ligands. The bridged Schiff bases have the following structure, which consists of numerous functional groups that can be altered depending on the situation.

Stable compounds with the carbon-nitrogen double bond (-HC=N-) are known as Schiff bases (SB).Imines are another name for them. (Imines are present in a variety of naturally derived compounds, including ancistrocladinine and chitosan-derived Schiff bases (Bringmann et al., 2004, Guo et al., 2007)). The amines attack(nucleophilic attack) the aldehyde groups to form the imine bonds. The imine group in these compounds has aided in the actions of these compounds (de Souza et al., 2007). Schiff bases typically have the equation RHC=Nar.

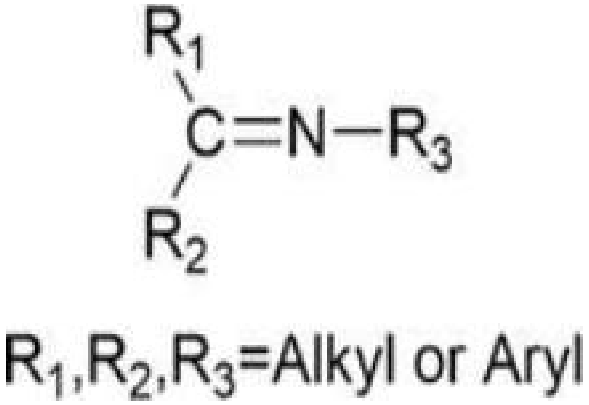


Figure 1: General representation of Schiff base

Aryl groups cause conjugation to occur in the system, which increases the stability of aryl Schiff bases while decreasing it for those containing alkyl substituents. According to Gomathi and Selvameena, the Schiff bases of aliphatic aldehydes are rather unstable and easily polymerizable, whereas those of aromatic aldehydes with efficient conjugation are more stable (Ashok et al,2015). The majority of Schiff bases have a delocalized -electron system, which causes them to have high nonlinear polarizabilities. Donor or acceptor groups frequently increase this effect. Because the basicity of the imine nitrogen's sp^2 hybridized nitrogen lone pair is well adapted to forming complexes with metal ions, while being lower than that of amines' sp^3 hybridization, schiff bases are among the most versatile nitrogen coordinating ligands.Due to their ease in forming stable complexes with the majority of transition metal ions, Schiff bases play significant roles in coordination chemistry (Atmaram and Kiran, 2011). Schiff bases are the source of the majority of the ligand complexes used in model studies (Bailey et al., 1986). Schiff bases share structural similarities with biological compounds that are found in nature. This improves their ability to explain the mechanism of biological reaction processes like transamination and racemination reactions.

Ketones do not readily produce Schiff bases when reacting with primary amines the way aldehydes do.

1.2.2. SYNTHESIS OF SCHIFF BASE

Schiff bases are synthesized by ough condensation reactions between aldehydes and amines. Hugo Schiff reported the first preparation in the 19th century (Schiff, 1864). Because the synthesis of Schiff bases is a reversible addition-elimination reaction, water elimination is critical for product formation. The most common reaction pathway for producing Schiff base is an acid catalyzed condensation reaction of an amine with an aldehyde or ketone under refluxing conditions. The first step in this reaction is an attack of an amine's nucleophilic nitrogen atom on the carbonyl carbon, resulting in a normally unstable carbinolamine intermediate. When the hydroxyl group is removed, a C=N bond is formed, and the product is known as imine. Many factors influence the condensation reaction, including the pH of the solution and the steric and electronic effects of the carbonyl compound and amine. Because the amine is protonated in acidic solutions, it cannot function as a nucleophile and thus the reaction cannot proceed. Furthermore, in very basic reaction conditions, the reaction is hampered because sufficient protons are not available to catalyze the elimination of the carbinolamine hydroxyl group. In general, aldehydes react faster than ketones in Schiff base condensation reactions because the reaction center of an aldehyde is less hindered sterically than that of a ketone. Furthermore, the extra carbon in ketone donates electron density, making the ketone less electrophilic than aldehyde. The various method of synthesizing Schiff base includes:

The conventional method: Hugo Schiff's 1864 synthetic method is known as the classical method, and it is still used today. This method involves the refluxing condensation of a carbonyl compound with an amine in organic solvents such as ethanol. The problem of water elimination led to the use of dehydrating agents. The presence of dehydrating agents to remove water produced normally promotes the formation of SBs. In the early 1990s, an in-situ method for water elimination using dehydrating solvents like tetramethyl orthosilicate or trimethyl orthoformate was developed (Love and Ren, 1993, Look et al., 1995). This method, however, is dependent on the use of highly electrophilic carbonyl compounds and strongly nucleophilic amines. Lewis acids such as $ZnCl_2$, $MgSO_4$, $NaHCO_3$, and H_2SO_4 have also been shown to activate the carbonyl group, catalyze the nucleophilic attack by amines, and dehydrate the system (Chakraborti et al., 2004).

Water-based method: The water-based method employs water as a solvent. The reactants are usually water soluble and are stirred at room temperature before being left to stand for 48-72 hours. The product obtained is re-crystallized from water. Water, as an abundantly available cheap solvent for reactions, is environmentally friendly and encouraged for green chemistry synthesis. The products are easily isolable, making reactants easier to handle. However, the method has limited application because most organic compounds are insoluble in water, whereas Schiff bases can also be hydrolyzed in water.

The grindstone method: The grindstone method of synthesis is a solvent-free reaction. Solvent-free reactions, such as those used in the synthesis of imines, Aldol, and Michael reactions, are quickly becoming the best synthetic method (Tanaka, 2003). The method entails grinding the reactants with a porcelain mortar and pestle until the mixture becomes pasty. Schiff bases form after standing for a few minutes to several days. The crude product is re-crystallized using appropriate solvents such as ethanol. The method was used to create bis-imine Schiff base from diamine and two equivalents of aldehyde (Van den Ancker et al., 2006). The use of Grindstone in synthesis has eliminated the need for heat and solvent in Schiff base synthesis. This can be done on a larger scale by using ultra high intensity grinding in a ball mill. The use of a cylinder reactor will result in improved conversion without the need for additional purification steps. This method is environmentally friendly and high yielding, but the conversion to product reaction time can be lengthy. However, this method cannot be used for reactants that are both liquid and solid.

Microwave irradiation method: Microwave irradiation was used to perform Schiff base synthesis. When using liquid reactants, the method uses very little solvent and can be solvent-free. Microwave-assisted condensation is typically performed in a microwave for a short reaction time, usually minutes. Several research groups have reported that synthesis of Schiff bases using microwave irradiation is fast and efficient (Yang et al., 2002, Yang and Sun, 2006, Gopalakrishnan et al., 2006, Kamaria et al., 2011). Environmental restrictions on emissions, as well as non-polluting and atom-efficient technologies, have increased interest in such synthetic techniques. Furthermore, there are several advantages to performing synthesis using microwave irradiation, including increased safety, shorter reaction times, and economic advantages due to the absence or use of very little solvent. Furthermore, solvent-free microwave processes are clean and efficient.

Ultrasonic irradiation method: Ultrasound irradiation has been regarded as a safe and useful method for the synthesis of organic compounds. Sonication can smooth out many homogeneous and heterogeneous reactions, increasing yield while decreasing selectivity. Ultrasonic irradiation makes use of an ultrasonic processor outfitted with a long probe that is immersed directly in the reaction mixture. This technique is more convenient and controllable than other methods. Under ultrasound irradiation, a large number of organic reactions can be carried out under milder conditions in shorter reaction times, resulting in higher yield. The disadvantage is that expertise is required, and the instrument is expensive.

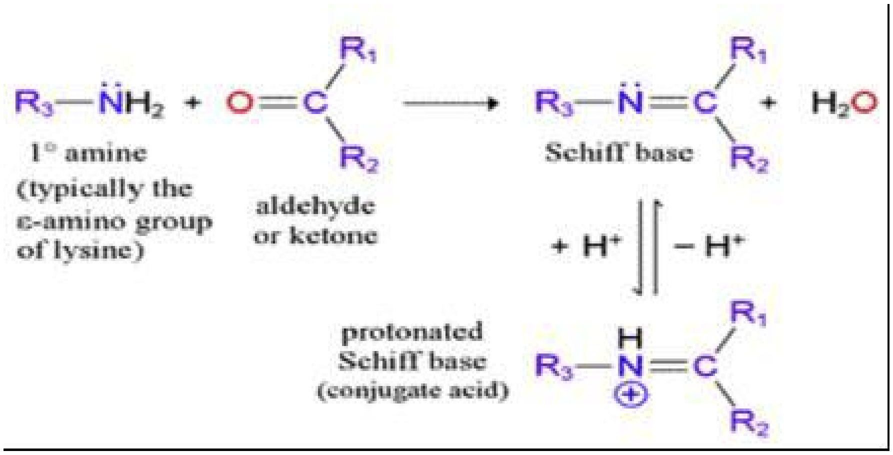


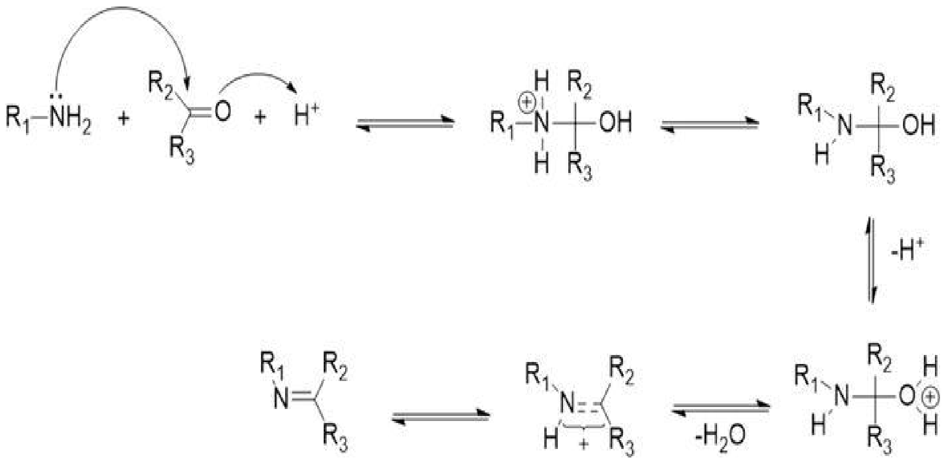
Figure 2: Schiff base synthesis

1.2.3 FORMATION MECHANISM SCHIFF BASE

The formation of a Schiff base from an aldehyde or ketones and amine is a reversible reaction that usually occurs under acid or base catalysis when heated. The dehydration of the carbinolamine is typically the rate-determining step in Schiff base formation, which is why the reaction is catalyzed by acids. Nonetheless, because amines are basic compounds, the acid concentration cannot be too high. If the amine is protonated and becomes non-neutral, equilibrium is pulled to the left, and carbinolamine formation is impossible. As a result, many Schiff base synthesises work best at mildly acidic pH. Base also catalyzes carbinolamine dehydration. This reaction is similar to the E_2 elimination of alkyl halides, except that it is not a concerted reaction. The formation is generally driven to completion by the separation of the product or the removal of water, or both. This is done in two steps, with an anionic intermediate in between. The Schiff base formation is actually a series of two types of reactions, namely addition followed by elimination (Ashok et al., 2015).

Condensation of aldehydes and amines occurs in a variety of reaction conditions and solvents. Methanol or ethanol are the most commonly used solvents in the preparation of Schiff base. Schiff base can be found at room temperature or in refluxing conditions. The presence of dehydrating agents is required for the formation of Schiff bases. If the synthesis is done in benzene or toluene, the water produced in the reaction can also be removed from the equilibrium mixture. The Schiff bases may degrade during the purification step. Hydrolysis can occur during Schiff base chromatography on silica gel. In such cases, it is preferable to crystallize the Schiff bases. Schiff bases are generally stable solids that can be stored safely. A large number of Schiff bases could be easily prepared because the amines and Aldehyde can be varied. The mono-, di-, tri-, and multi-dentate chelating Schiff bases are designed to match the binding environments of metal ions (Gomathi and selvameena).

The reaction of aliphatic or aromatic aldehydes or ketones with aliphatic or aromatic primary amines is the most widely used method discovered by Schiff for the preparation of Schiff bases. The reaction of carbonyl compounds with primary amines yields Schiff bases in two steps. A carbinolamine intermediate is formed in the first step by condensation of the carbonyl group with the primary amine, and a Schiff base is formed in the second step by dehydration of the intermediate.



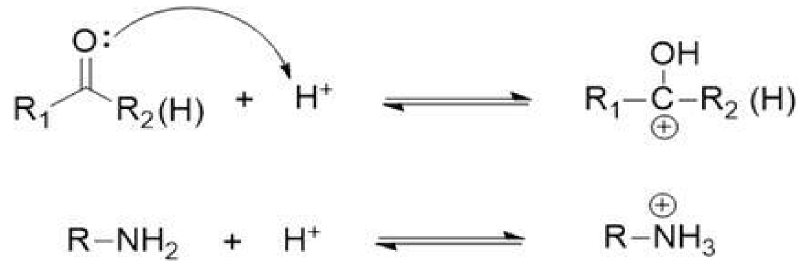
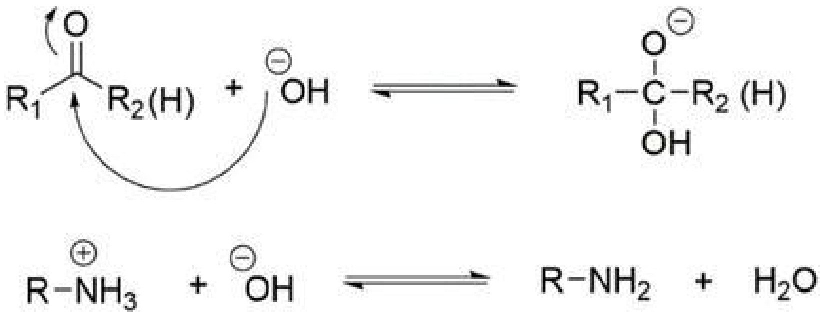


Figure 3: Condensation of carbonyl compounds with amines.

The formation of Schiff base is a pH-dependent reaction. Because the amine will form salt at low pH, the free amine concentration decreases, and the fast addition step slows down and becomes the step that determines the rate of the reaction mechanism. When acidity decreases, the addition step becomes faster and the elimination step becomes slower.The optimal pH is between these two extremes (pH 3-4). This pH is suitable for both initiating the nucleophilic addition reaction and performing the elimination reaction at a sufficient rate.

Figure4 : Increase in electrophilic power and decrease in nucleophilic power in acidic medium.

Figure5: shows a decrease in electrophilic power and an increase in nucleophilic power in basic medium.



Substitution has a significant impact on the stability of Schiff bases. Because small-molecular-weight aliphatic imines with no substituents on the nitrogen atom polymerize easily, detailed information on these imines is lacking. Schiff bases with aryl substituents are more stable and easily synthesized due to the electron feeding of the imine bond via ring conjugation, whereas those with alkyl substituents are relatively unstable, take a long time to synthesize, and polymerization is observed. Because they are less sterically hindered, aldehydes are more reactive than ketones in the formation of imine. Furthermore, in ketones, groups attached to the carbonyl carbon donate electrons, reducing the electrophilic character of the carbonyl carbon and causing the reaction to proceed more slowly. As a result, while aldehydes and primary amines can easily form Schiff bases, ketones can be difficult to obtain. Many factors must be considered in order to obtain Schiff base from ketones, including selecting a solvent that can form an azeotrope mixture with the water released during the reaction, selecting a catalyst, selecting the appropriate pH range, and selecting the appropriate reaction temperature. High temperature, a long reaction time, and a catalyst are all required to produce Schiff base from aromatic ketones. Aromatic aldehydes and ketones can combine to form highly stable Schiff bases. Aromatic aldehydes react with amines at low temperatures and in a suitable solvent environment. It has been shown that the reaction rate of aromatic aldehydes with aromatic amines increases in the presence of an electron-withdrawing substituent in the para position of the aldehyde and decreases in the presence of an electron-withdrawing substituent in the para position of the amine. While water must be removed during the synthesis of Schiff base from aromatic ketones, there is no need to remove water during the synthesis of Schiff base from aldehydes and dialkyl ketones. While water must be removed during the synthesis of Schiff base from aromatic ketones, there is no need to remove water during the synthesis of Schiff base from aldehydes and dialkyl ketone.

1.2.4.SCHIFF BASE METAL COMPLEXES

Metal complexes are made up of a central metal atom or ion surrounded by several atoms, ions, or molecules known as ligands. Metal complexes' physicochemical properties have paved the way for their widespread application in science. Schiff base metal complexes (SBMCs) are formed by reacting Schiff base ligand with transition metal ions. The high affinity of Schiff bases for chelation of transition metal ions is used in the preparation of their complexes (Cozzi, 2004). Transition metal complexes of Schiff bases are one of the most adaptable and thoroughly studied systems in bioinorganic chemistry (Mounika et al., 2010). According to reports, the rapidly developing field of bioinorganic chemistry is focused on the presence of coordination compounds in living systems (Raymond and AbuDari, 1977). Thus, Schiff base metal complexes may serve as models for biologically important species (Jayabalakrishnan and Natarajan, 2001). Previous research (Hodnett and Dunn, 1972; Mounika et al., 2010) revealed that metal chelation increases the activity of some bioactive compounds. In-vitro antibacterial studies on ciprofloxacinimines and their complexes with Cu(II), Ni(II), Co(II), and Zn(II) revealed that the metal complexes outperformed the uncomplexed ligands (Imran et al., 2007).

Schiff bases are metal ion selective and form complexes by transferring electrons from the active ends they contain to the metal. Schiff bases are a good nitrogen donor ligand. These ligands donate one or more electron pairs to the metal ion during coordination compound formation. Schiff bases that donate more than one electron pair can form highly stable 4-, 5-, and 6-ring complexes. A second functional group containing a displaceable hydrogen atom must be found as close to the azomethine group as possible. This group is preferably the hydroxyl group.

1.2.5 CHARACTERIZATION OF THE SCHIFF BASE METAL COMPLEX

The complexes' bonding nature and stereochemistry were deduced from elemental analyses, IR, UV-Vis, 1H NMR, mass, electronic spectra, magnetic susceptibility, and conductivity measurements, and their thermal stability was confirmed by thermogravimetric analysis (TG). These spectroscopic methods have been applied to the study of Schiff bases and their metal complexes. All of these elucidate different aspects of the structure.

Infrared spectroscopy: Infrared spectroscopy studies the interaction of infrared radiation with matter. It is used to measure the vibrational frequencies of bonds in a molecule by scanning over a range of frequencies. Because each bond has a characteristic frequency, any frequency that matches the characteristic frequency of a bond will absorb infrared radiation. As a result, the IR spectrometer can be used to detect functional groups and provide information about the type of bonds present. The wavelength of light absorbed by a compound determines the type of bond it has. The wavelength becomes shorter as the frequency increases.

1H-NMR spectroscopy: Nuclear magnetic resonance (NMR) spectroscopy is the study of molecular structure via the interaction of an oscillating radio-frequency electromagnetic field with a collection of nuclei immersed in an external magnetic field. The carbon-hydrogen framework of an organic compound can be identified using nuclear magnetic resonance (NMR) spectroscopy. The number of signals in a 1H NMR spectrum indicates the type of protons in a molecule, and the position of the signal indicates the type of protons present. These protons can be shielded or unshielded. A shielded proton requires a high applied field strength for absorption, whereas a deshielded proton requires a lower applied field strength for absorption. Shielding shifts the absorption upfield, while deshielding shifts the absorption downfield. The presence of substituent groups influences the field strength around the protons. Electron withdrawing substituents reduce the electron density in the vicinity of the proton, resulting in deshielding from the magnetic field, whereas electron donating substituents increase the electron density in the vicinity of the proton, resulting in shielding from the magnetic field. As a result, the signal for these protons occurs at a lower magnetic field (high) than the signal for the more shielded protons (low), which occurs at a higher magnetic field.

Electronic absorption spectroscopy and magnetic moment measurements: Because molecules and atoms have electronic transitions, uv-vis spectroscopy measures the response of a sample to ultraviolet and visible ranges of electromagnetic radiation. Electronic transitions found in organic compounds include, and n electrons, while complexes contain d and charge transfer transitions. Excitation of a molecule from its electronic ground state to an electronic excited state corresponds to light absorption in the near-infrared, visible, or ultraviolet regions of the spectrum. Electronic transitions in organic compounds are typically observed in the 200-400 nm range. The first two bands in the 204-270 nm range are assigned to the excitation of the aromatic ring's -electrons (*). The third band observed in the wavelength range 257-295 nm is usually due to a transition between the -orbital largely localized on the central C=N bond. An intermolecular charge transfer is responsible for the fourth band in the wavelength range 305-360 nm. A fourth band was occasionally observed due to polar solvents within the wavelength range 435-440 nm attributed to intermolecular CT between the solvent and the molecule (Soliman, 1997).

Metal complexes show electronic transitions as well. The spectra of transition metal complexes are determined by the transition of unpaired electrons from the ground state to an excited state. Transitions between the central atom's split d-levels can occur, resulting in the d-d or ligand field spectra. The atomic overlap in metal—ligand bonds allows electrons to pass from the central atom to the ligand and vice versa. The effect of ligands on the energies of the metal ions' d orbitals affects the transitions. Because octahedral, squareplanar, and tetrahedral fields split d orbitals in different ways, the geometry has a significant effect on d-d transitions in a metal complex. Complexes with octahedral geometry have the orbital energy levels t_{2g} (dxy, dyz, dxz) and eg (dx_2- y_2, dz_2). They could be Jahn-Teller distorted octahedral complexes in which two trans metal-ligand distances are shorter or longer than the other four, resulting in a tetragonal distortion. According to the Jahn-Teller theorem, a non-liner molecule is unstable in a degenerate state and will distort to remove the degeneracy, so the distorted complex is more energetically favorable than a regular octahedral complex (Housecroft and Sharpe, 2008). Electronic absorption spectra are frequently very useful in evaluating the results of other structural investigation methods. Two electrons will enter the a1g (dz_2) and the other into the b1g (dx_2-y_2) for copper(II), compared to three electrons in the eg for regular octahedral complex. A shoulder on the d-d band of the electronic spectrum results from the overlapping of two closely spaced absorption bands caused by electronic transitions from the dxy, dyz, and dxz levels to the a_{1g} and b_{1g} levels. Copper(II) (d_9) is almost always found in a distorted ligand environment, with the metal ion surrounded by two elongated bonds opposite each other and four shorter bonds in the xy plane. When the trans ligands are removed, a square planar geometry is obtained. Square planar complexes are particularly common at the end of the transition-metal series, especially for ions with d_8 and d_9 configurations. Many squareplanar complexes of palladium and platinium exist. The energy levels in a square-planar complex are eg (dxz, dyz), b_{1g} (dx_2- y_2), and t2g (dxz, dyz) (dxy). For square planar complexes with dx2-y2ground state, three spin-allowed transitions are possible: 2B1g 2A1g (dx2- y2 dz2.....v1), 2B1g 2B2g (dx2- y2 dxy.....2), and 2B1g 2Eg (dx2- y2 dxz, dyz. (Patel et al., 2011). Strong field ligands typically form square-planar complexes, while weak field ligands form octahedral and tetrahedral complexes. The orbital energy levels for tetrahedral complexes are lower e (dx2- y2, dz2) and higher t2 (dxy, dyz, dxz). Because the smaller-crystal field splitting makes nearly all tetrahedral complexes high spin, the bands in the spectra should be lower wavenumber (longer wavelength) than those in octahedral complexes. At the same concentration, the tetrahedral complexes are far more intense than their octahedral counterparts. This is due to the fact that they lack a center of symmetry. A charge transfer transition has a higher energy absorption than a d-d transition. The electron moves between orbitals, i.e. from metal to ligand or ligand to metal. Ligand metal charge transfer is observed in high oxidation state metal ions and lone pair ligand donors, whereas metal ligand charge transfer is obtained in low oxidation state metal. The spectral data of transition metals provide useful information about the structure of complexes. The spectra of numerous transition metal complexes containing various Schiff-base ligands have been described in the literature (Kamounah et al., 1998, Herzfeld and Nagy, 1999). The spectra show electronic transitions typical of ligands and metal ions in coordination. These spectra are sensitive to the type of ligand and have proven useful in identifying specific complex species. In the visible region of regular tetrahedral and near tetrahedral Co(II) complexes, only one d-d transition [4A2(F) -4T1(P)] was observed. These transitions have also been reported for tetrahedral [Co(NCS)4]2-at 615 nm

(Lever, 1984). Several authors have investigated changes in spectra caused by the addition of metal ions. Some have also interpreted the d-d transitions of such metal complexes.

Thermal analysis of Schiff base metal complexes: Thermal analysis (TA) is a group of techniques in which changes in the physical or chemical properties of a sample are monitored against time or temperature while the temperature of the sample is programmed. The temperature program could include fixed-rate heating or cooling. Thermal analyses include thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermal mechanical analysis (TMA), temperature resolved X-ray diffraction, thermomagnetometry, thermoconductometry, and dilatometry. TGA and DSC are the two most commonly used thermal analyses. Thermal stability of materials, estimated lifetime of a product, decomposition kinetics of materials, moisture and volatile content of materials are obtained from TGA studies, whereas the DSC graph provides the glass transition temperature (Tg), crystallization temperature (Tc), melting temperature (Tm), and sample purity of the materials. As thermal energy is applied to the sample, its enthalpy rises and its temperature rises by an amount determined by the sample's specific heat for a given energy input. The specific heat of a material changes slowly with temperature in a specific physical state, but changes abruptly when the state changes. Thermal energy can cause physical or chemical processes in the sample, such as melting or decomposition, as well as a change in enthalpy, the latent heat of fusion, heat of reaction, and phase transformation.

1.2.6 APPLICATION OF SCHIFF BASE AND ITS METAL COMPLEXES

Schiff bases, which are derived from an amino and carbonyl compound, are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been extensively studied. The C=N linkage is essential for biological activity in azomethine derivatives; several azomethines have been reported to have remarkable antibacterial, antifungal, anticancer, and diuretic activities. Schiff bases have numerous applications in the food industry, dye industry, analytical chemistry, catalysis, fungicidal, agrochemical, and biological activities. With the rising prevalence of deep mycosis, there has been a greater emphasis on the development of new and more effective antimicrobial drugs with low toxicity. Due to their preparative accessibility and structural variety, schiff-base complexes are regarded as one of the most important stereochemical models in main group and transition metal coordination chemistry. A large number of Schiff-base complexes have potential biological interest and have been used as more or less successful models of biological compounds. They not only played a seminal role in the development of modern coordination chemistry, but they can also be found at critical points in the development of inorganic biochemistry, catalysis, and optical materials.

Schiff's bases have also been shown to have a wide range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties. Schiff bases and their metal complexes play an important role in the industries. Poly Schiff bases synthesized from amine terminated natural rubber (ATNR) and glyoxal have been shown in the polymer industries to improve natural rubber aging resistance (George et al., 1993). When natural rubber is photodegraded in solution in the presence of ethylenediamine, amine terminated natural rubber (ATNR) is formed.

We can divide reactions in which Schiff base can be used as a precursor into four groups:

- Addition of an organometallic reagent or hydride to a C=N bond to form an asymmetric C-C bond.
- The hetero Diels-Alder reaction is used to create six-membered nitrogen-containing heterocyclic compounds.
- The use of chiral salen metal complexes in asymmetric synthesis.
- The Staudinger reaction with ketene yields biologically important -lactams.

1.2.7. IMPORTANCE OF SCHIFF BASES AND THEIR METAL COMPLEXES

The mechanisms of biochemical reactions can now be explained thanks to advances in spectral methods. It has been discovered that some reactions in living organisms take place on Schiff bases, which eliminate the toxic effects of aldehyde and amine components and bind free metal ions. Schiff bases are becoming increasingly important as a result of their properties, which allow them to be used in biological systems, chemical catalysis, medicine and pharmacy, chemical analysis, and new technologies. To summarize why Schiff bases have such a large working area:

- The template effect can also be used to synthesize Schiff bases. This procedure directly returns the designed complexes. When reacted with a different metal salt, these complexes can also undergo transmetalation reactions. This method ensures that complexes that cannot be obtained by other methods are obtained with sufficient purity and yield.
- Schiff bases can form stable complexes with almost all metals because they generally contain additional donor groups such as N, O, S, and P. In addition to these characteristics, they play important roles in biological systems.

- Schiff bases are easily synthesized from carbonyl compounds and primary amines and can be functionalized in a variety of ways using appropriate groups.
- They can form polyamine derivatives that are more flexible and less sensitive to hydrolysis when treated with suitable reducing agents. These reduced compounds contain NH groups that can be further functionalized using appropriate synthetic procedures.
- They create modified catalysts and different designed surfaces by bonding to a suitable support, such as silica.
- Special ligands can be formed by binding groups such as crown ether, macrocyclic thioether, and polyaza derivatives to form selective systems capable of bind different metal ions.
- Because of the interaction of metal chelates with the DNA helix, they can be used to create new models for diagnosis and therapy.

Furthermore, because of their photochromism, they can be used in a variety of fields such as controlling and measuring radiation intensity, image systems, and optical computers. Because the metal complexes of these compounds are colored, they are used as pigment dyestuffs in the dye industry, particularly in textile dyeing. Furthermore, they are widely used in the perfume and pharmaceutical industries. These compounds also have properties such as synthetic oxygen carrier and intermediate in enzymatic reactions. They are also used as spectrophotometric reagents in analytical chemistry because they react selectively and specifically to certain metal ions. They can be used in aircraft construction, television and computer screens, and digital clock displays by utilizing the liquid crystal feature found in some metal complexes.

1.2.8 SCHIFF BASE AS A COORDINATING LIGAND

A ligand is an ion or molecule that donates a pair of electrons to the central metal atom or ion to form a coordination complex. The term ligand comes from Latin and means "to tie or bind." Ligands can be anions, cations, or neutral molecules. Ligands act as Lewis bases (donate electron pairs), while central metal atoms act as Lewis acids (electron pair acceptor). The type of bonding between metal and ligand varies from covalent bond to ionic bond. Schiff bases are macrocyclic or macro-acyclic ligands that contain both nitrogen and oxygen donors and are frequently polydentate in their coordination ability. However, the donor's identity can be changed between sulfur, phosphorus, nitrogen, and oxygen to change the donor properties and thus the ligand's coordination abilities. Schiff bases are sometimes synthesized as compartmental ligands, in which binding at one site influences a change in conformation at another site on the molecule for cooperative complexation with two or more metal ions metals. Schiff bases have traditionally been prepared by the condensation reaction of a formyl- or carbonyl-containing derivative with primary amine groups in the presence of templating metal ions such as alkaline earth cations.

1.2.9 CLASSIFICATION OF SCHIFF BASE LIGANDS AND METAL COMPLEXES

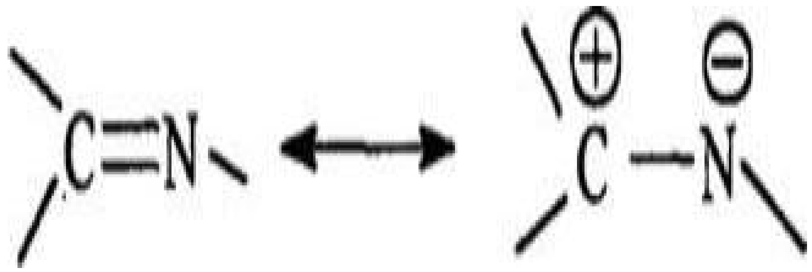
Complexation of these Schiff base derivatives with various metal ions revealed the ability to form mono-, di-, and polynuclear metal complexes in which they behaved as monodentate, bidentate, or tridentate ligands depending on the positions and number of electron donating groups. When a ligand's donor sites occupy two or more coordination positions on the same central metal ion, a complex with a closed ring is formed. Chelation is the phenomenon that causes rig formation, and the ring that forms is known as a chelate ring. Schiff bases primarily have nitrogen donor atoms, though many also have mixed donor capabilities. In general, the donor nature of the ligand is determined by both the type of aldehyde or ketone used and the nature of the primary amine.

The donor atoms of a Schiff base metal complex are used to classify it. Some of the metal complexes encountered depend on the type and number of donor atoms they contain.

1.3.0 PHYSICAL PROPERTIES OF SCHIFF BASE

Schiff bases are often solids that are pigmented and transparent. Because of their exact melting points, they are utilized to determine metal quantities and to identify carbonyl compounds. In Schiff bases, the carbon-nitrogen double bond rotates more easily than the carbon-carbon double bond, allowing stereoisomers to convert into one other. The reason for this is that because nitrogen is more electronegative than carbon, polarization develops in the azomethine bond.

Figure6 : The azomethine bond is polarized.



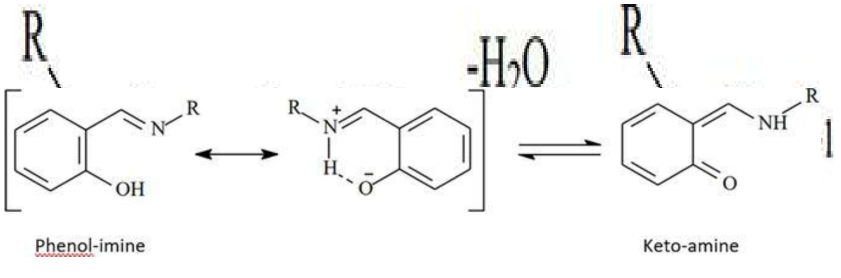
With a few exceptions, the stereoisomers of Schiff bases cannot be isolated due to the very small energy difference between them. Stereoisomers are isolated when only an electronegative group is linked to the nitrogen atom, because this group reduces the ease of rotation around the azomethine bond. Because the electronegative group connected to the nitrogen atom in the azomethine group pushes the nitrogen atom's negative charges toward the carbon, polarization decreases and the nature of the covalent double bond increases. Because of the unshared electron pairs on the nitrogen atom and the electron donating property of the double bond, all compounds containing an azomethine group have basic features. Schiff bases have poorer basic characteristics than equivalent amines. The reason for this is that while the nitrogen atom in amines experiences sp3 hybridization, when the imine structure is produced, this hybridization transforms into sp2 hybridization. Because the (s) character increases with hybridization, the basicity decreases dramatically. The CN system is a weak chromophore that absorbs in the UV range. Absorption is shifted to the visible area when phenyl groups are conjugated. When an aromatic ring has a deactivating substituent, such as a halogen, the wavelength of absorption lowers. In general, aryl alkyl ketimines absorb at concentrations between dialkyl and diaryl ketimines. The CN system's IR stretch bands are commonly noticed at 1610-1635 cm1 and CN+'s at 1665-1690 cm1.

1.3.1 CHEMICAL PROPERTIES OF SCHIFF BASE

The characteristics of Schiff bases vary depending on the substituents linked to the azomethine group. When an electronegative group is linked to the nitrogen atom, the stability of the azomethine molecule increases. The finest example is that oximes with hydroxyl groups on the nitrogen atom, as well as phenylhydrazones and semicarbazones with NH groups, are far more resistant to hydrolysis than Schiff bases with alkyl or aryl substituents on the nitrogen atom. Although Schiff bases are alkali resistant, hydrolysis in an acidic environment separates them into amine and carbonyl molecules. The reaction of Schiff base production is reversible. One mole of water is generated as a result of the reaction, and the water in the surroundings alters the reaction's direction to the left. As a result, the reaction is typically carried out in solvents where water may be removed from the environment via distillation, resulting in the formation of an azeotrope. The reaction is completed when amines having an electronegative atom with unpaired electrons in the nitrogen atom are used, and because hydrolysis does not occur, Schiff bases can be separated with great efficiency.

Figure7: the Schiff base formation reaction.

The tautomeric transformations that occur depending on the polarity of the solvent and the hydrogen bonds that occur in the molecule define the structures of Schiff bases. In terms of Schiff base stability, the nonplanar structure is the favored shape. Quantum mechanics



calculations have also corroborated this conformation.

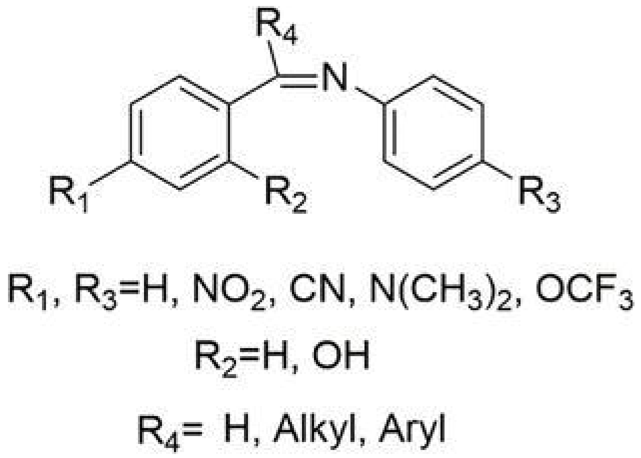


Figure 8: Schiff base preferred configuration.

According to the research, there are two types of tautomer forms in Schiff bases created by utilizing aldehydes containing an ortho hydroxy group: phenol-imine and ketone-amine. Spectroscopic approaches such as 13C-NMR, 1H-NMR, UV-Vis, and X-ray crystallography were used to confirm the presence of these two tautomeric structures.

Figure 9: Schiff base tautomeric structure.

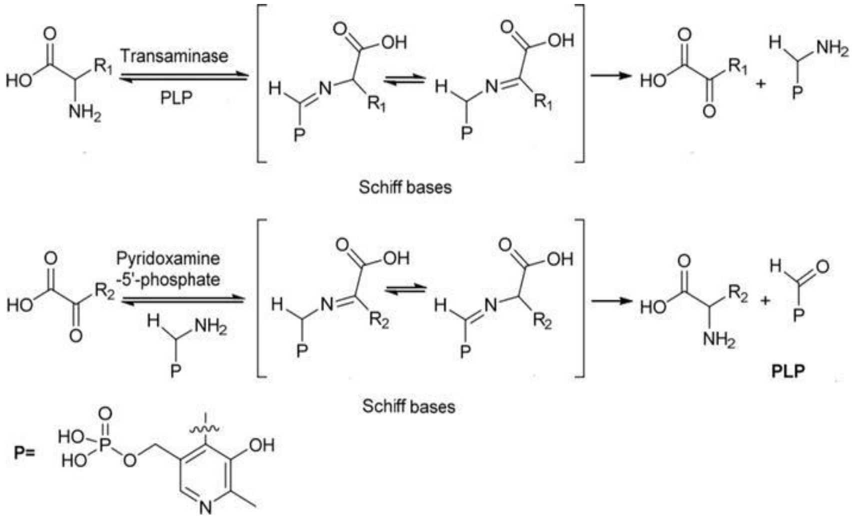
In studies with Schiff bases prepared from 2-hydroxy-1-naphthaldehyde and some aromatic and aliphatic amines (ammonia, methylamine, and phenylamine), the keto form was found to be dominant in polar solvents like chloroform, while the enol form was found to be dominant in nonpolar solvents like ethanol.

1.3.2: BIOLOGICAL ACTIVITIES OF SCHIFF BASES

Schiff bases and metal complexes are essential components of biological systems because of their anticancer, antibacterial, antifungal, and antiviral characteristics.The most important biological function of Schiff bases is their role in amino acid biosynthesis, which is one of the most fundamental processes in life. Schiff bases are critical intermediates in the production of -amino acids ($RCHNH_2COOH$), which are employed in the creation of proteins in animals. In some situations, if there is insufficient necessary amino acid in the meal, the body transforms an excess amino acid to the amino acid it requires via a transamination mechanism and it is transferred to the keto acid via a succession of Schiff bases in this process

Figure10:Transamination reaction from amino acid to keto acid via Schiff bases.

Furthermore, Schiff bases have been shown to be present in a wide range of natural, semisynthetic, and synthetic chemicals and to be required for their biological action.



1.3.3: CHITOSAN

Chitosan, a natural

cationic polysaccharide, has gotten a lot of interest as a useful, renewable, nontoxic, and biodegradable biopolymer for a variety of uses, particularly in pharmaceutics, food, and cosmetics. Because of its anticancer, immunoenhancing, antibacterial, and hypocholesterolemic qualities, chitosan has been created not only as artificial skin, absorbable surgical suture, and wound healing accelerator, but also as new physiological materials in the medical area. These functions have been shown to be chemical structure and molecular size dependent. As a result of its high molecular weight and highly viscous character, this natural polysaccharide's applicability is limited due to its low solubility in acid-free aqueous conditions. Studies on chitosan modification have expanded in recent years, since efficient usage of marine biomass resources has become an environmental priority, as has a better use of chitosan. Based on our current research and the recent literature, this review focuses on the modification of chitosan by enzymatic hydrolysis and various chemical processes, in combination with pharmaceutical and biomedical applications, particularly in hypocholesterolemic, immunoenhancing, homeostasic, and anticancer functions.

The alkaline treatment affects the proportion of the two monosaccharide units in chitosan. Individual chains, in general, have an essentially linear structure that undergoes one full twist every 10.1-10.5 along the chain axis. Because each monosaccharide unit is chiral, polymer chains rotate to the left or right. As a result, chitosan could be classified into three crystal types:, and, which could be identified using an X-ray model and NMR spectra. Among these, the -type is the most common type obtained from shrimp and crab crust.

At the C-2, C-3, and C-6 locations, chitosan has three types of reactive functional groups: an amino/acetamido group, as well as both primary and secondary hydroxyl groups. The amino contents are the key variables influencing variances in their structures and physicochemical qualities, and their distribution is random, making intra- and intermolecular hydrogen bonds simple to form.

Using the reactive activity of hydroxy- and amino groups, many new chitosan derivatives have been synthesized. The amino group, in particular, has nucleophilic properties, allowing for the easy formation of imine by reaction with aldehyde or corresponding amide derivatives in acylating reagents; in acidic solution, the amino groups exhibit alkaline properties and receive protons to generate salts with cationic polymer properties. Furthermore, the amino functional group has been linked to chelation, flocculation, and biological processes.

However, it is crucial to note that different chitosans have distinct biological activities, and not all biological activities are found in one type of chitosan. Chemical modification and enzymatic hydrolysis were used to create each unique form of bioactive chitosan for potential pharmacological and medical applications.The reactive groups found in chitosan includes a primary amino group (C_2) and primary and secondary hydroxyl groups (C_6, C_3). Glycosidic bonds and the acetamide group can also be considered functional groups. These functional groups allow for a great number of modifications, producing polymers with new properties and behaviours.Chitosan derivatives have been produced, aiming to improve chitosan's properties, such as solubility or biodegradability, or to introduce new functions or properties. For instance, solubility has been improved in water aqueous media by deacetylation, depolymerization, or quaternisation among other processes. New chitosan activities have been reported after its modification, for example,6-O-sulphated chitosan promotes neuronal differentiation while phosphorylated chitosan inhibits corrosion.The field of chitosan chemistry is wide.

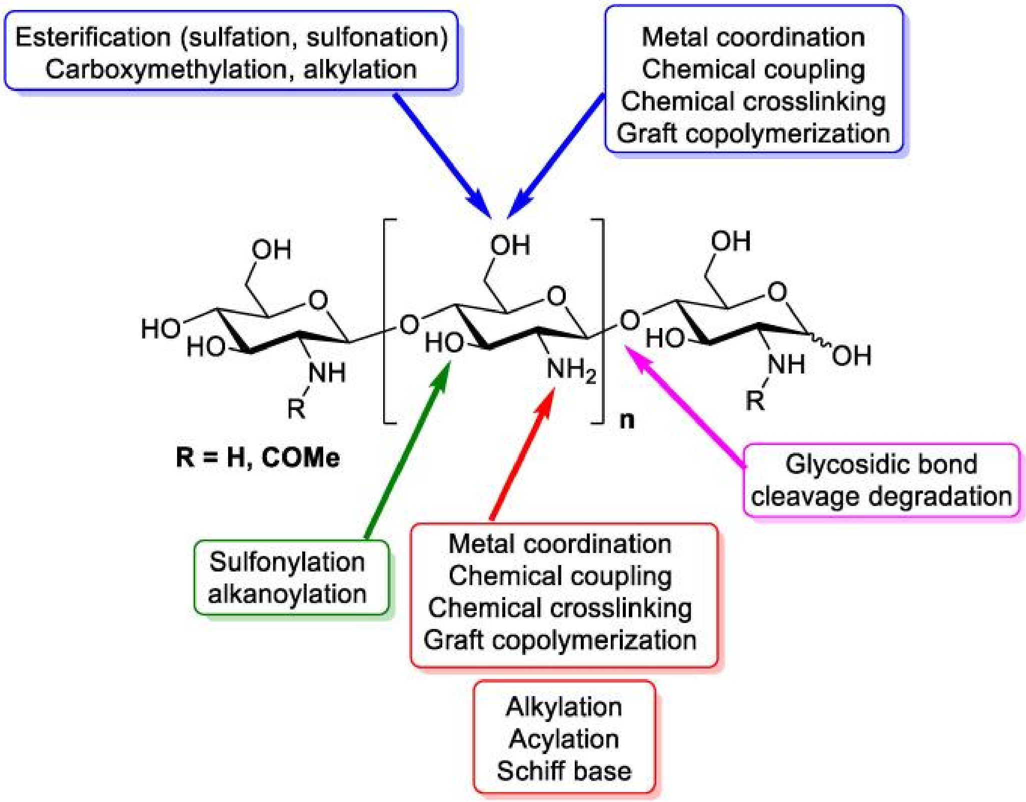


Figure 11: Functional group of chitosan

1.3.4:TRANSITION ELEMENTS AS METAL COMPLEXES

The periodic table has transition metals in the center. They are found in the metallic state as well as a variety of compounds with varying characteristics. Many of these compounds are ionic or network solids, but some are molecular in nature, with various atoms organized around a metal ion. These are known as transition metal complexes or coordination complexes. They are frequently brilliantly colored chemicals that can be quite useful as catalysts or even medications. Transition metals are typically found as positively charged ions, or cations, due to their low electronegativity. These metal ions do not appear on their own; rather, they attract additional ions or molecules to themselves. These species form coordination complexes with the metal ions.

Coordination complicated equations constantly provide you insights regarding the structures. The material contained within the square brackets is invariably one of the ions. There are several things related to the transition metal in that section. The ligands are the things that are attached to the transition metal; the part outside the square brackets tells you what the counterions are; these are there to balance the charge of the ion inside the square brackets. Individual atomic ions, such as chloride anions (Cl-) or potassium cations (K+), are frequently used as counterions. So, when you see K_2 in the formula, it means that the potassium atoms are not linked together; they are two distinct potassium ions: 2 K+. Similarly, the Cl_3 at the end of a formula does not refer to a collection of three chlorine atoms crowded together; it refers to three distinct chloride ions, 3 x Cl-. Polyatomic ions can sometimes act as counterions to these complexes; this is especially prevalent with anions. They are most commonly oxoanions, which are atoms with a number of oxygens bonded to them. Nitrate (NO_3-) and sulfate (SO_2-) are two of the most common examples; both ions have been recognized for hundreds of years. Tetrafluoroborate (BF_4-) and hexafluorophosphate (PF_6-) are two anions from the twentieth century.

Transition-metal complexes have been assigned coordination numbers ranging from 1 to 12, with the most prevalent being 2, 4, and 6.

CHAPTER 2

2.0. MATERIALS AND METHOD

2.1. MATERIALS

2.1.1. APPARATUS

- 250ml beaker

- 250ml conical flask
- 100ml graduated pipette
- Plastic funnel
- 100ml measuring cylinder
- 500ml Buchner flask
- Buchner funnel size 3
- Condenser
- 250ml RBFQ
- Vacuum pump
- Oven
- Magnetic stirrer
- What man filter paper

2.1.2. REAGENTS

- Acetic acid
- Methanol
- Benzaldehyde
- Chitin from shrimp
- NaoH
- Distilled water

2.2. METHODOLOGY

2.2.1. PREPARATION OF CHITOSAN

2.2.2.Preparation of chitosan from snail shells

The snail shells were thoroughly washed to remove sand, dirt and other impurities and then dried. These shells were dried under the sun for 48 hours and later oven dried for 4 hours at 100^0C. These dried snail shells were crushed with a mortar and then ground with a grinding machine so as to pulverize the shells into fine powder. After the snail shell powder was obtained, three major steps were followed in order to extract chitosan. These steps include deproteinization, demineralization and deacylation.

2.2.3 Deproteinization

80 g of snail shell powder was weighed into a conical flask, 100 ml of 40% NaOH was added. The resulting mixture was boiled and stirred at 100^0C for 2 hours in a water bath. The solution was then filtered and washed with distilled water so as to make the pH of the solution neutral. This was determined by using a red litmus paper to check if the base was completely washed away. The neutral residue obtained was then dried in an oven at 100^0C for 3 hours. In this process the protein content of the shell is withdrawn from the main chemical structure.

2.2.4 Demineralization

After deproteinization, the weight of the sample recovered was about 57g. 30 ml of 5 % of 1 M HCl was added to the deproteinized sample. The resulting mixture was then boiled and stirred for 45 minutes at 100^0C in a water bath. The mixture was then filtered and washed with distilled water in order to make the pH of the solution neutral. This was determined by using blue litmus to check the acidity of the mixture. The neutral residue (chitin) obtained from this process after filtration, was then dried in an oven at 100^0C for 2 hours. An organic matter calcium carbonate is eliminated in dilute acidic medium.

2.2.5 Deacetylation

The residue (chitin) formed from the demineralization process was soaked in 500 ml of 5 % of NaOH. The resulting mixture was then boiled at 100^0C for 2 hours in a water bath and cooled for 50 minutes at room temperature. The mixture was placed on a magnetic stirrer for 4 hours at 30^0C, filtered, washed with distilled water to a neutral pH. This was determined by using red litmus to check if the acid was completely washed away. The mixture was filtered through a filter paper to get chitosan as a residue. The chitosan formed was then oven dried at 90^0C for 24 hours. The weight of chitosan obtained from the process was 40 g.This process involves partial removal of acetyl group from chitin structure.

2.2.6. Preparation of chitosan Schiff base

1gram of Chitosan was dissolved in 100ml of an aqueous acetic solution(1%) at room temperature. Then 5ml of benzaldehyde dissolved in 50ml of ethanol was added to the chitosan solution. This reaction mixtures were let to react at temperature of 55^0C with stirring for 3hours. The resulting pale orange yellow gels of Schiff base was filtered, washed several times with ethanol to remove any unreacted aldehyde and dried in vacuum oven at 70^0c. The obtained powder was kept in a dessicator over silica gel.

2.2.7. Preparation of Schiff base metal complex.

25ml of hot ethanolic solution of Schiff base was mixed with 25ml of hot ethanolic solution of co(ii) sulphate. pH was adjusted by adding ammonium hydroxide to form solid chelate. The mixture was refluxed after stirring for 2-3hrs. The resulting precipitate was filtered and washed with distilled water and ethanol several times to remove any unreacted aldehydes, using a Buchner funnel. The obtained powder was kept in a dessicator over silica gel.

2.2.8. Physical and thermal analysis of chitosan, the Schiff base and its metal complex

Solubility: 1g of chitosan Schiff base was weighed and put into a 100ml of water in a 500ml beaker and allowed to rest, then the solution was observed for dissolution. Chitosan Schiff base was observed to dissolve in water.

Melting point: Firstly, the sample was dried in a desiccator. Then a small portion of sample was ground in a mortar.A water bath was prepared and the temperature was monitored until it is 100^0C, 1g of chitosan Schiff base was added into a test tube , the test tube was placed into the water bath and observed till the substance turned liquid, the first temperature was taken immediately with a thermometer when the substance started melting and when the substance was fully melted the second temperature was taken.

Colour: After each synthesis of Schiff base and its metal complex the colour was observed and noted.

CHAPTER THREE

RESULT AND DISCUSSION

3.1. RESULTS AND DISCUSSION

In the course of this study, the amine functional group in chitosan was synthesized with benzaldehyde to form a Schiff base which was further synthesized with a $Co^{2\pm}$ to form a metal complex. From the above physical characterization, it is gathered that the solubility, colour and melting point of a substance helps to characterize a substance as either a pure or impure substance.

Solubility properties

Chitosan exhibits low solubility in water and most organic solvents because of strong intermolecular and intramolecular hydrogen-bonding interactions among chitosan macromolecular chains. Chitosan reacts with aldehyde(benzaldehyde) to form chitosan schiff base, which becomes soluble in water. Another suggestion is based on the ability of Chitosan Schiff base to form a complex with metal, for instance,Co^{2+}; these metals are important for bacterial metabolic processes and growth, and must test highly soluble in water. The concept and measure of solubility are extremely important in many sciences besides chemistry, such as geology, biology, physics, and oceanography, as well as in engineering, medicine, agriculture, and even in non-technical activities like painting, cleaning, cooking, and brewing. Most chemical reactions of scientific, industrial, or practical interest only happen after the reagents have been dissolved in a suitable solvent. Water is by far the most common solvent. Solubility is the ability of a substance, the solute, to form a solution with another substance, the solvent. Insolubility is the opposite property, the inability of the solute to form such a solution.

Compounds	Solubility in water
Chitosan	Insoluble
Chitosan Schiff base	Soluble
Schiff base metal complex	Soluble

Fig 12: The result of the solubility test for chitosan, chitosan SCHIFF base and its metal complex.

Determination of Melting point

Compounds	Melting point

Schiff base	230^0C
Metal complex	233^0C

Fig 13: The result of the melting point and observation of the colour for Schiff base and it's metal complex.

For the schiff base: lmmediately the substance started melting the reading was taken to be 225^0C and when the substance was fully melted the readings were taken again to be 235^0C. The average of the readings were then taken to determine the actual melting point which is 230^0C. The literature melting point of Schiff base and its metal complex ranges from 230^0C - 233^0C. For the metal complex, the first reading was taken to be 230^0C and the second reading was taken to be 236^0C, taking the mean of both reading the melting point is said to be 233^0C.Comparing the melting point point from this experiment to the literature melting point, it is shows that the Schiff base and its metal complex is a pure compound because of the increasing melting point. The melting point of the complex was observe to be higher than the Schiff base, this suggests change in composition of the Schiff base due to complexation.

Colour properties

COMPOUNDS	COLOUR
Schiff base	Pale yellow
Schiff base metal complex	dark red

Fig14: the colour observation taken during the synthesis

The colour was observed to change from pale yellow to dark red when the Schiff base was synthesized with a metal.The colour transformation is due to the reaction of the transition metal with the Schiff base ligand.

3.2. CONCLUSION

The new Schiff base was synthesized from benzaldehyde and amine functional group of chitosan under magnetic stirrer method.The synthesized Schiff base and it's metal complex was physically characterized. And the Schiff base was observed to be a solid crystal, soluble in water and having sharp melting point. The physical characterization of these compound where necessary to help identify the compounds after comparing the results with the literature values

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