

An Updated Review on Versatile Application of Schiff Base Metal Complexes

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ABSTRACT

Schiff-base metallic complexes have attracted immense scientific attention due to their unique properties and use in industrial and biological areas. Schiff bases are an essential chemical compound category produced by condensation of primary amines and aldehydes or ketones. Their recognized characteristics include applications in organic synthesis, chemical and biological sensing, agricultural chemistry, polymer and resin industries, coating, catalysis, coordination chemistry, and drug development. The $-C=N-$ (imine or azomethine) functional group in Schiff bases is a crucial pharmacophore for developing and synthesizing lead bioactive chemicals. The wide range of biological effects of Schiff-bases has piqued the interest of many in medicinal chemistry. These complexes show various biological activities, such as antioxidant, cytostatic, and antibacterial/fungal effects. Additionally, they exhibit exceptional catalytic activity for a range of processes. This study focuses deeply on the chemistry, production, history, and uses of Schiff-base ligand-based metallic complexes, emphasizing the compounds' biological and industrial purposes. This review provides an overview of current circumstances and future directions of research in the field of inorganic chemistry, which may be extremely beneficial to researchers and those working in this field.

Key-words: Schiff base, metal complexes, azomethine, pharmacophore, biological activities, antifungal, antibacterial, antioxidant, cytostatic

INTRODUCTION

Macronuclear or macroacyclic ligands containing nitrogen and oxygen donors that play a part in coordination and often polydentate due to their coordinating characteristics are collectively referred to as Schiff bases. These ligands contain a functional group that is either azomethine ($-C=N-$) or an imine. Aldehydes or ketones condense with a primary amine to generate these compounds. This arrangement replaces the $-C=O$

group with the $C=N-R$ group. Schiff bases with aryl groups are more stable than those with alkyl groups. Schiff base's structure and condensation mechanism are provided (Fig. 1). Thus, they show a variety of biological actions, including antiviral, antifungal, antibacterial, antiproliferative, and anti-inflammatory activities ^[1]. They have piqued the scientific community's interest greatly because of how easily they can be synthesized and complexed with metals. The conventional manufacturing process for Schiff bases and metallic complexations is as follows: Schiff bases based on N_2O_2 metallic complexes, including salicylaldehyde and diamines, have attracted much interest. Their structures include hetero-atoms N, O, and S serve as the active sites for synthesizing novel physiologically active molecules and aid in creating diverse pharmacophore types ^[2].

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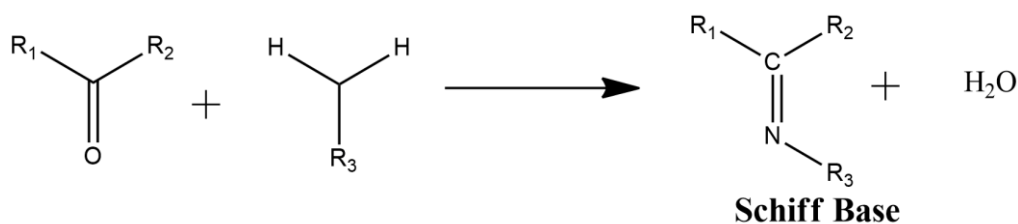


Fig. 1: Condensation Reaction of Schiff Base

In designing new drugs, condensation of two or more molecules in organic reactions is frequently used to discover new substances with higher biological applications. Schiff bases are essential because they may engage in diverse commercial and biological applications by forming stable metal complexes with different oxidation states. Schiff bases and their metal complexes have been evaluated because of their unique and important functions, such as catalytic qualities, the ability for reversible binding to oxygen, photochromic attributes, and their capacity to form complexes with some transition metals. Furthermore, they actively participated in biological modelling activities involving sensors, corrosion inhibitors, and catalysis [3–6]. Schiff bases have a broad range of functions in the biochemistry fields, including antibacterial, antituberculosis, anticancer, and antioxidant [7–10].

The study of hydrazones has gained popularity due to its characteristics, including physiological activity, the ability to produce higher coordination numbers in stereochemistry, the ability to deport as neutral or deprotonated ligands, coordination ability due to the presence of additional donor sites, and numerous applications in analytical chemistry [11]. Many hydrazone derivatives are used as stabilizers because of their fascinating bioactivity, which includes antimalarial, anticonvulsant [12], anti-inflammatory [13], and analgesic properties [14]. They are also involved in the regulation of plant development. Because of their azomethine functional group, Schiff bases have exceptional biological and catalytic activity. In addition to increasing their efficiency for biological applications, they had active donor sites in their structure that helped build coordination compounds with the metal ion [15]. Transition metal complexes enhance Schiff bases' biological activities and efficiency because of their large abundance and ability to form metal-organic amalgam [16].

A carbonyl and an amine condensation is done at different processing conditions and solvents in the conventional Schiff bases synthesis. Dehydrating agents thereby expedite the condensation process [17]. The Schiff base ligands process linking appropriate amines, aldehydes, and ketones have been widely used since their discovery. To create metallic complexes from Schiff base ligands, one often combines the Schiff base with easily accessible metallic complexes such as metal amides, alkyls, acetates, or halides. For catalytic applications, this technique is appropriate and easy to use [18]. Schiff bases are composed of an active imine bond that gives them an affinity for metallic ions through N, O, and S, as discussed in previous subsections.

However, this study is anticipated to act as a model for upcoming polls. The history of Schiff bases and their metallic complexes is given in the first section of the review. An overview of the general methods, including green methods, for synthesizing Schiff bases and their metal complexation is presented in the second section. Also emphasized are the most notable instances of this class of chemicals that have been documented in the literature. The third and last sections of the study focus on the most current uses of Schiff bases based on metallic complexes, as well as their useful applications in biology and catalysis.

Schiff Base Metal Complexes-Biological Significance-

Further research in this field is highly attractive because of the broad potential for biological, analytical, and industrial uses of Schiff base ligands and their complexes. These are used in Biochemistry, agriculture, medicine, food, pharmaceuticals, and photo-responsive biomaterials. Their applications include ion transport via membranes, phase transfer processes, isotope separation, and biomimicry of metalloenzymes such as hemethrin and haemoglobin [19]. Analgesic, lipid-lowering, antioxidant, antiviral, antifertility, anti-HIV,

antiproliferative, diuretic, antibacterial, antifungal, antitumor, antioxidant, anticonvulsant, and enzyme inhibitory properties are just a few of the biological, electrochemical, and catalytic qualities that Schiff base metal complexes have demonstrated [20].

Antimicrobial Application- Gram-positive and gram-negative human pathogenic microorganisms have been employed as antibacterial agents. *Streptococcus pneumonia*, *Enterococcus faecalis*, *Staphylococcus aureus*, and *Bacillus subtilis* are some gram-positive

bacteria. *Xanthomonas campestris*, *Proteus vulgaris*, *Pseudomonas aeruginosa*, and *E. coli* are examples of gram-negative bacteria. *Geotricum candidum*, *Aspergillus fumigates*, *Candida albicans*, and *Syncephalastrum racemosum* are a few fungi employed for their antifungal properties. Ni(II), Cu(II), and Zn(II) complexes of Schiffbase ligand generated from the amino acids L-tryptophan and 2,4-dihydroxybenzaldehyde have been reported by some researchers in Fig. 2 shown below.



Fig. 2: Antimicrobial activity of Gram-positive and gram-negative pathogenic microorganisms

The complexes of Ni (II), Zn (II) and Cu (II) have been shown to have higher antibacterial effects against *P. aeruginosa*, *S. aureus*, *E. coli*, *E. faecalis*, and *P. vulgaris*. The results demonstrate that metal complexes show more strong antibacterial activity than ligands. The chelation hypothesis is responsible for the antibacterial action of the metal complexes. The metal ions that chelate the ligand enhance its antibacterial properties beyond those of the ligand alone. The core metal ion's lipophilic nature is enhanced and the ligand's chelating capability decreases its polarity. The sharing of the metal ion's positive charge with the ligand and the dispersion of the pi-electron throughout the full chelating molecule is responsible for the reductions in polarity. As a result, the lipid layer of the cell membrane would be penetrated. According to the impermeability of the cells, different compounds have been observed to be effective against different microorganisms. Furthermore, the concentrations shown are significant, with an increase in concentration corresponding to a rise in the degree of

inhibition [20]. As a result, the chemical becomes more active.

Antioxidant Application- An efficient method for studying the radical scavenging of specific substances is the DPPH (2, 2-diphenyl-1-picryl-hydrazyl) radical scavenging activity assay, a type of antioxidant screening. Because it contains an odd electron and may take an electron or an H-atom, the DPPH is a static free radical that can change into a static, diamagnetic molecule. This is why it exhibits an absorption band at 517 nm in the UV spectrum. The absorption band stoichiometrically diminishes when the electrons are coupled to accept electrons or H-atoms. The investigation of different compound's capacity to act as free radical scavengers is mostly acquired by this shift in absorbance. As a result, the compound's more active antioxidant application coincides with an accelerated absorbance decline. The scavenging's output statistics were compared to the antioxidant standards used. Using DPPH reagent and free radical scavenging, the Schiff

base and its metal complexes were described using the Blois technique ^[21].

The Schiff base's ability to scavenge free radicals and its metal complexes was tested using the DPPH radical and L-ascorbic acid as references, as seen in Fig. 3. The percentage of scavenging activity was calculated by using samples at several concentrations (i.e., 10, 20, 50, 100, 150, 200, 250, and 300 mg/ml) in ethanol. The DPPH was then supplemented with 40µl+2.96ml. The samples were incubated for 30 minutes at room temperature and then their absorbance was measured at 517 nm along with blank sample. Samples with lower IC₅₀ values show greater antioxidant activity. The capability of the sample compounds' H-atoms or electrons to be donated is shown by the bleached purple-colored ethanol solution of DPPH. The final findings demonstrated the excellent radical scavenging abilities of all the assessed samples at various concentrations ^[22].

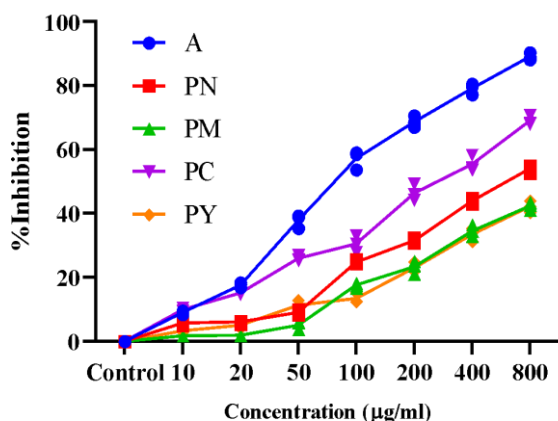


Fig. 3: Antioxidant activity (free radical scavenging)

Anti-inflammatory activity- HRBS method- *In-vitro* HRBC (Human red blood cell) stabilization method was used to evaluate the efficacy of various drugs in reducing the severity of a certain disease. A 10 mL human blood sample was drawn and put into heparin-containing centrifuge tubes. Equal parts of Alsever solution (0.42% sodium chloride, 2% dextrose, 0.05% citrus extract, 0.8% sodium citrate, and 100 mL of purified water) and the collected blood were mixed and the mixture was centrifuged using isosaline (0.85% saline solution made by dissolving 8.5 g of sodium chloride in water).

Subject the material to autoclaving for 15 minutes at a temperature of 121°C. Chilled to the ambient temperature, an equal volume of mixtures in four distinct concentrations (10, 20, 50, 100 µg/mL) was

added to 1 mL of HRBC solution. All the test mixtures were incubated at 37°C for 30 minutes and then subjected to centrifugation. The hemoglobin concentration in the supernatant solution was calculated at a wavelength of 560 nm using a spectrophotometer ^[23]. The level of hemolysis was subsequently determined using the provided formula.

% of hemolysis =

$$\frac{[\text{Absorbance of control} - \text{Absorbance of sample}]}{\text{Absorbance of control}} \times 100$$

Alpha-amylase enzyme inhibition assay- The dinitrosalicylic acid (DNS) approach was used to measure the alpha-amylase inhibitory activity. A few minor adjustments were made to the previously described procedure. The test mixture comprised 500 µL of 0.5 mg/mL amylase solution, generated using a pH 6.9 sodium phosphate buffer containing 0.05 M of amylase concentration. Furthermore, the mixture was supplemented with test chemicals at 25, 50, 100, and 150 µM molarities. After that, the combination was incubated for ten minutes at 37°C. After the pre-incubation period, 500 µL of the buffer's 1% starch solution was added to each tube. After that, the tubes were incubated for an additional fifteen minutes at 37°C.

A 1.0 mL DNS reagent was added to produce the reaction, and after that, the test tubes were incubated for five minutes in a boiling water bath and then allowed to cool to the ambient temperature. Subsequently, 10 mL of deionized water was added to dilute the reaction setup, and the absorbance was taken at 540 nm. The control group had complete amylase enzyme activity. As a reference inhibitor, acarbose was used and assessed for each test sample ^[24]. According to the stated measurement conditions, an alpha-amylase unit is the quantity of catalyst needed to create 1 mM of maltose per minute at 37°C. The equation used is;

$$\% \text{ inhibition} = \frac{[\text{Absorbance of Control} - \text{Absorbance of Test}]}{\text{Absorbance of Control}} \times 100$$

The IC_{50} values were obtained using non-linear regression analysis on plots of percent inhibition against log inhibitor concentration, using the mean inhibitory values. The approach above was employed to get the IC_{50} values by using various doses of test samples. and the results were reported as Mean \pm Standard Deviation (SD) and the studies were performed in triplicate.

Kinetics of inhibition- The Michaelis-Menten and Lineweaver-Burk plots assess how much an agent inhibits alpha-amylase. During the evaluation, a 200 μ L sample of the material was incubated with 0.5 mg/mL of α -amylase. The starch (substrate) content ranged from 0.2 to 5 mg/mL. After 10 minutes of incubation at 37°C, and after that the compound had been heated for 5 minutes and 1.0 mL of DNS was used to stop the reaction. Using a

maltose standard curve and spectrophotometry, the amount of reducing sugars was calculated and then translated into reaction velocities.

A dual-axis plot was generated, with 1/V on the y-axis and 1/[S] on the x-axis, to analyze the relationship between reaction velocity (V) and substrate fixation [S]. This figure allowed us to determine the type of restraint exerted by the samples on the action of α -amylase ^[25].

Catalytic Application- Schiff base metal complexes are used as catalysts in homogeneous and heterogeneous reactions, even though their activity depends on the presence of metal ions and ligand binding sites. They are used as catalysts for chemical reactions, such as oxidation, Aldol, polymerization, coupling, cycloaddition, and hydrosilylation of ketones.

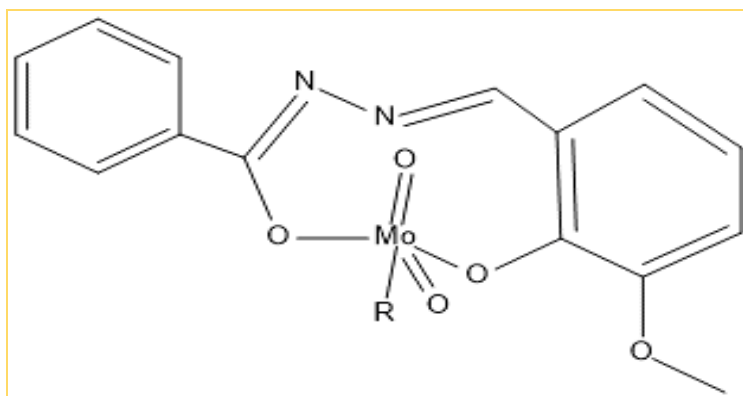


Fig. 4: Schiff base metal complex using as catalyst.

Schiff base metal complexes make oxidizing alcohols, sulphuration, epoxidation of alkanes, and alkane oxidation simple. An appropriate carbonyl molecule and amine substitution can alter catalysts' steric and electrical behaviour. The electrophilic reaction of indole with aldehyde to produce methane derivatives has been reported to benefit from the catalytic activity of a catalyst based on molybdenum ^[26]. It has been shown that the metal complex catalyst exhibits more activity than the parent Schiff base ligand catalyst.

Schiff Base Metal Complexes in Sensors- Owing to their vital importance in biological and industrial processes, medicine, catalysis, environmental sciences, and humanities, molecular recognition sensing of ions is one of the most fascinating and active areas of supra-

molecular chemistry study. Chemosensors are a good way to find metal ions since they are very straightforward and extremely selective. Coordination sites on those chemosensors bind (Fig. 5) the guest in a way that causes colour changes to be shown by the signal in g unit. Deprotonation in these receptors is thought to cause the colour shift. In addition to being sufficient to produce colour change on its own, the organic base speeds up intramolecular change transmission by conjugation, which results from ions-induced proton dissociation of the chromophore. A colorimetric response is produced by the ions dislocating the coordinated chromophore ^[27].

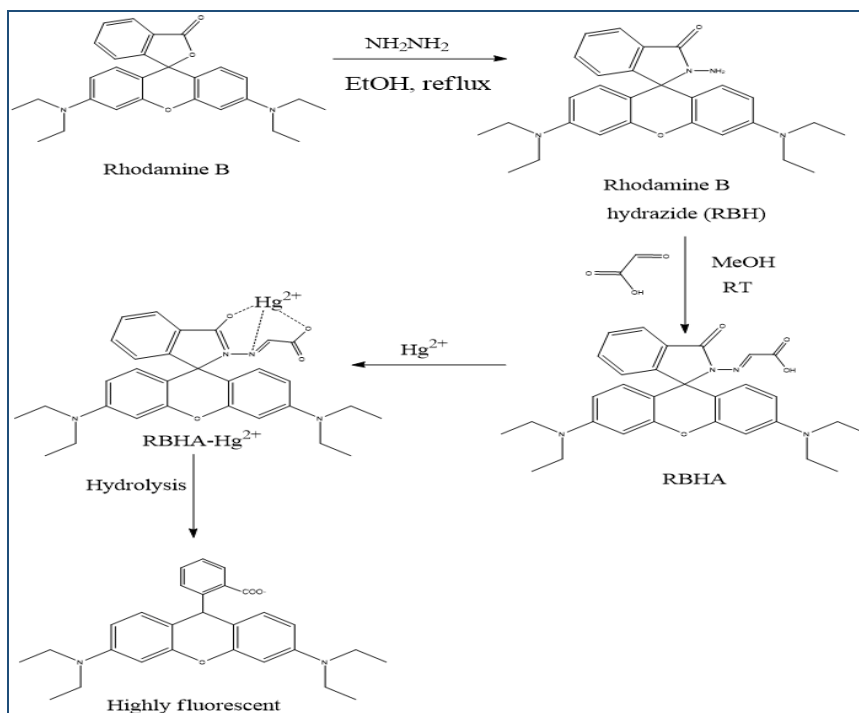


Fig. 5: Hydrolysis reaction of the Chemosensors RBHA

The human body is constantly exposed to heavy metals, which cause cellular disruption and toxicity. The body eliminates heavy metals through the kidneys, spleen, or liver. In contrast to other molecules, metal is eliminated quite slowly. In excretory organs, a small number of cysteine-rich proteins help to retain these heavy metal ions for extended periods. Due to altered cellular function, this metal storage causes organ damage. Using Schiff base-based sensor molecules can greatly aid heavy metal ion detection in water samples. Some researchers developed and built a new fluorescent chemosensor called RBHA with simplicity. Glyoxylic acid was included in the structure of the compound to make rhodamine hydrazide more water-soluble. The rhodamine glyoxylic acid conjugate, which is very fluorescent, is generated when Hg^{2+} assisted hydrolysis is detected using the chemosensors RBHA [28,29].

CONCLUSIONS

The pharmacological characteristics of Schiff bases and their ability to make complexes with transition metal ions make them an exceptionally significant family of organic chemical compounds. There has been a significant increase in attention to Schiff base complexes over the past several decades, partially because of their wide range of biological applications and their potential in researching and developing novel medicinal pharmaceuticals.

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Data collection- Priti Yadav, Dr. Kiran Rangari, Dr. Divya Verma, Dr. Ranjeet Kumar Nirala

Data analysis and interpretation- Priti Yadav, Dr. Kiran Rangari, Dr. Divya Verma, Dr. Ranjeet Kumar Nirala

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Article editing- Dr. Kiran Rangari, Dr. Divya Verma, Dr. Ranjeet Kumar Nirala

Final approval- Prof. Anjana Sarkar, Dr. Kiran Rangari, Priti Yadav

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