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A short review on chemistry of Schiff base metal complexes and their applications

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Abstract

Schiff bases and their complexes are flexible compounds synthesized from the condensation of an amino compound with carbonyl compounds and extensively used for industrial purposes and also show a broad range of biological activities including antibacterial, antifungal, antiviral, antimalarial, antiproliferative, anti-inflammatory, anticancer, anti-HIV, anthelminthic 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 behavior. Development of a new chemotherapeutic Schiff bases and their metal complexes is now attracting the attention of medicinal chemists. This review compiles the various synthesis procedures and application of Schiff bases and their metal complexes.

Schiff bases are aldehyde- or ketone-like compounds in which the carbonyl group is replaced by an imine or azomethine group. They are widely used for industrial purposes and also exhibit a broad range of biological activities. This short review compiles examples of the most promising antimalarial, antibacterial, antifungal, and antiviral Schiff bases. An overview of synthetic methodologies used for the preparation of Schiff bases is also described.

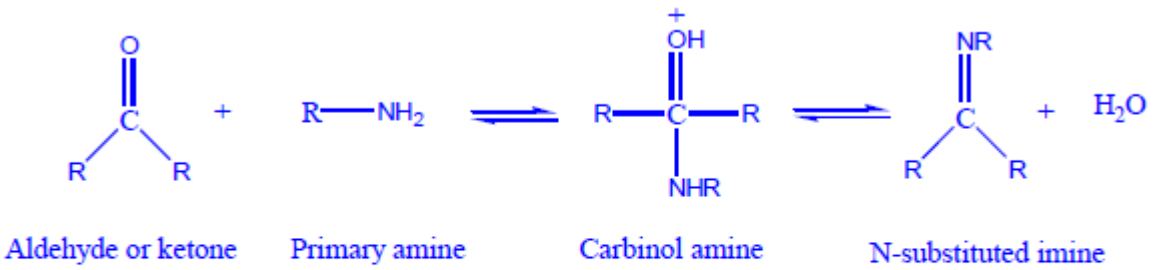
Keywords: Schiff bases, Metal complexes, catalytic application, Fluorescent, ribonucleotide reductage

1. Introduction

Schiff bases played an important role as ligands even a century after their discovery in coordination chemistry [1]. Schiff bases are an important class of ligands in co-ordination chemistry [2]. Schiff bases are derived from the condensation reaction of aromatic/aliphatic aldehydes and amines and form stable complexes with different

transition metal ions are still relevant to be of great interest in inorganic chemistry, although this topic has been extensively studied [3]. Schiff bases and their metal complexes have been shown to be promising leads for both synthetic and structural research due to their relatively simple synthesis and structural diversity and have been widely investigated, due to their incredible chemical properties and applications in various areas. The chelating ability and biological applications of metal complexes have attracted remarkable attention and they can work as models for biologically important species [4]. A number of Schiff bases containing the imino functionality have been shown to have a wide range of biological activities, including antibacterial, antifungal, antidiabetic, antitumor, antiproliferative, anticancer, anticorrosive and anti-inflammatory activities [5]. It is believed that the biological activity is related to the hydrogen bonding through the imino group of Schiff bases with the active centers of the cell constituents. Metal-imine complexes have been widely investigated due to catalytic and herbicidal utilization [6]. Thiosemicarbazones are a class of compounds obtained by condensation of thiosemicarbazide with suitable aldehydes or ketones and they are also applicable in fields of inorganic chemistry. They are used as a chelating ligand for the formation of metal complexes because of variety of flexible donor sets of sulfur and nitrogen [7]. People are working from last many years on the synthesis and characterization of transition metal complexes with thiosemicarbazones because of their wide range of medicinal applications and their abilities to coordinate with the transition metal ions which is highly desirable [8]. The properties of thiosemicarbazones have received considerable attention because of their variable bonding modes, promising biological implications, structural diversity, and ion-sensing ability [9].

Schiff bases are condensation products of primary amines and carbonyl compounds and they were discovered by a German chemist, Nobel Prize winner, Hugo Schiff [10]. Structurally, Schiff base (also known as imine or azomethine) is an analogue of a ketone or aldehyde in which the carbonyl group (C=O) has been replaced by an imine or azomethine group (Figure-1) [11]. A Schiff base or Schiff's base is a type of chemical compounds containing a carbon-nitrogen double bond as functional group, where the nitrogen atom connected to aryl group or alkyl group (R) but not hydrogen. The Schiff base is synonymous with an azomethine. These compounds were named after Hugo Schiff on honor and have the following general structure:



Scheme 1.2: Formation of Schiff base

Pharmacology of Schiff base transition metal complexes;

The involvement of variety and extent of metal ions has been recently appreciated, but it has very long history in medicine, toxicology and medicine. For instance transition metals like Zn, Mn, Fe, Co, Ni, Cu and Mo among the transition metals are very essential to life and involved in various biological activity.[12]. The action of platinum believed to be on DNA the quantity of drug administered is in milligrams of quantities. Platinum interacts with DNA and the remaining excess amount makes complexes with cellular and extracellular fractions. [13]

Physical techniques and better understanding of inorganic chemistry reflects the more issues can be addressed with significant chances of success. Therefore, it is primarily important to concentrate on basic principles developed for transition metal ions for considering individual metal systems. The hydro peroxidation of lipids is catalysed by a class of iron containing dioxygenases known as lipoxygenases possessing structure of cis-1, 4-pentadiene. They are very much widespread in animals and plants. They are very much widespread in animals and plants. The number of lipoxygenase isoenzyme carry out the metabolism of leukotrienes and prostaglandins .The formation of hydroperoxide is catalysed by hydroperoxides as the biosynthesis of several inflammatory mediators in the first step, which leads to leukotriene synthesis.

The large non-haem iron -containing enzymes like lipoxygenases use molecular oxygen for the deoxygenation of arachidonic acid for the deoxygenation of arachidonic acid for the formation of hydroperoxides due to significance of such compounds, in a no. of diseases; the extensive study has been conducted on lipoxygenase [14]. The enzyme inhibitors are the substances which intercede natural substrates of enzymes, especially in their conversion. The enzyme inhibition study of reported compounds is involved in the investigation of the choice of drugs in the pharmaceutical research area. The targets of anti-HCV and anti-HIV drugs are the proteases of HCV (NS3protease) and HIV, which are involved in the replication of viruses. The declared inhibitors in genetically engineered plants are also targets of plant pathogens “[15]”.

Even though there has been tremendous progress in the drug discovery process, infectious diseases continue to emerge. This might be due to an increase in resistance and susceptibility of microbes towards drugs; therefore, it is a great challenge to develop effective drugs to treat microbial infections. Quinolinyl oxadiazoles and quinoline Schiff bases are considered to be promising therapeutic agents which have huge importance in medicinal chemistry [16].

The Ni (II) complex of the ligand showed comparable antioxidant activity to the standard BHT. The DNA binding results show that the compounds bind to CT-DNA via intercalative mode.

The synthesized compounds have potent cleavage activity without any external reagents, but the cleavage activity is more when H2O2 is added as external oxidising agent. Cu (II) complex displayed good anti-proliferative activity compared to the remaining compounds. From all the results, Cu (II) and Zn (II) complexes can be used as a promising antitumor agents in vivo to inhibit the DNA replication in the cancer cells and not allow the tumour for further growth [17]

2,2-Diphenyl-2-picrylhydrazyl (DPPH) assay is widely used for assessing the ability of radical scavenging activity, and it is measured in terms of IC50 values. DPPH is a wellknown radical and a scavenger for other radicals. Therefore, DPPH radical was reduced in the presence of an antioxidant. The results revealed that the ligand (IC50 = 1.35 μg/ mL (5.62 μM)) and its Ni (II) complex (IC50 = 0.79 μg/mL (1.74 μM)) exhibited significant activity. By increasing the concentration of the compounds, the scavenging activity was also increasing [18]

Biological activities of Schiff bases

1. Antimalarial activity

Malaria is a neglected disease that still causes serious public health problems. Every year, approximately 500 million people are afflicted by the disease, of whom around 1–3 million die, 90% of who in sub-Sahara Africa are primarily children [19].Malaria is currently found in more than 100 countries throughout Africa, Latin America, Asia, and Oceania. Human malaria is mainly caused by four species of Plasmodium (P. falciparum,P. vivax, P. ovale, and P. malariae). The female mosquito of the Anopheles genus is the vector of Plasmodium [19].The search for new drugs, vaccines, and insecticides to prevent or treat this disease is clearly a priority.

Schiff bases have been shown to be interesting moieties for the design of antimalarial agents. Ancistrocladidine is a secondary metabolite produced by plants from the families

Ancistrocladaceae and Dioncophyllaceae that present an imine group in its molecular scaffold. Compound 1 has been shown to be active against P. falciparum K1 and 3D7. The minimum inhibitory concentrations (MIC values) of ancistrocladidine necessary to completely abolish P. falciparum K1 and 3D7 growth were 0.3 and 1.9 lg/mL, respectively. Interestingly, compound 1 was 90- and 10-fold more selective to P. falciparum K1 and 3D7, respectively than to rat skeletal myoblast L-6 cells. Rathelot et al. described the synthesis of Schiff base-functionalised 5-nitroisoquinolines and investigated the in vitro activity of these compounds against an ACC Niger chloroquine resistant P. falciparum strain. Schiff base 5 (Fig. 3) was the most effective antimalarial agent among the synthesised 5-nitroisoquinoline derivatives. The concentration of compound 5 necessary to inhibit P. falciparum growth by 50% (IC50) was 0.7 lg/mL. Under the same experimental conditions the IC50 value for chloroquine was 0.1 lg/mL [20].

2. Antibacterial activity

The increase in the mortality rate associated with infectious diseases is directly related to bacteria that exhibit multiple resistance to antibiotics. The lack of effective treatments is the main cause of this problem. The development of new antibacterial agents with novel and more efficient mechanisms of action is definitely an urgent medical need [41]. Schiff bases have been pointed to as promising antibacterial agents. For example, N-(salicylidene)-2-hydroxyaniline is effective against Mycobacterium tuberculosisH37Rv, exhibiting an MIC value of 8 lg/mL [21].

The selectivity of compound 4 was checked by performing experiments with J774 macrophages. No cytotoxic effect on J774 macrophages was observed for compound 4, even when it was tested at concentrations as high as

1000 lg/mL. More than 80% of macrophage cells were viable at such experimental conditions, demonstrating the high selectivity of compound.

The synthesis and antimicrobial activity of a series of Schiff bases derived from the condensation of 5-chloro-salicylaldehyde and primary amines has recently been reported [42]. The 5-chloro-salicylaldehyde-Shiff base derivatives 6–15 (Fig. 3) were most active against at least one of the evaluated bacterial species. Pseudomonas fluorescence was the strain most sensitive to compounds 6–11 and 13–15, with MIC values ranging from 2.5 to 5.2 lg/mL. The MIC value for the reference drug kanamycin against the same bacterial strain was 3.9 lg/mL. The Schiff bases 6, 7, 9–11, 14, and 15 presented MIC values in the range of 1.6–5.7 lg/mL against Escherichia coli, while the MIC value for kanamycin was 3.9 lg/mL. Bacillus subtilis was sensitive to the Schiff base 14 only (MIC= 1.8 lg/mL). The MIC values for compounds 6 and 7 against Staphylococcus aureus were, respectively, 3.1 and
1.6 lg/mL [22].

3. Antifungal activity

Fungal infections are not usually limited to the superficial tissues; indeed, a significant increase in life threatening systemic fungal infections has been reported. The fundamental reason for this is the increasing number of patients at risk, including those with advanced age, major surgery, immunosuppressive therapy, acquired immunodeficiency syndrome (AIDS), cancer treatment, and solid-organ and hematopoietic stem cell transplantation [23].

The search and development of more effective antifungal agents are mandatory and some Schiff bases are known to be promising antifungal agents. Alternaria brassicae and Alternaria brassicicola are phytopathogenic fungi that severely affect the production of most Cruciferous crops (broccoli, cauliflower, mustard, turnip, cabbage, rape, and radish). N-(Salicylidene)-2-hydroxyaniline 4 (Fig. 2) at the concentration of 500 ppm inhibited the growth of these fungi by 67–68% [61]. Compounds 2 and 3 (Fig. 2) are examples of chitosan-derived Schiff bases with antifungal activity. They inhibited the growth of Botrytis cinerea and Colletotrichum lagenarium by 26–33% and 35–38% when used at 1000 ppm, respectively.

Overall, studies evaluating the effect of Schiff bases on phytopathogenic fungal growth have
been modest and deserve more investigation. lated and hepatitis C human immunodeficiency diseases have been the drawback of vaccine approaches . Viral diseases are life-threatening for immunocompromised patients and a Prompt treatment is required to overcome this problem. Although there are many therapeutic options for viral infections, currently available antiviral agents are not yet fully effective, probably due to the high rate of virus mutation. They may also present any of a number of side effects. Salicylaldehyde Schiff bases of 1-amino-3-hydroxyguanidine tosylate are a good platform for the design of new antiviral agents [24]. In fact, from a set of different 1-amino-3- hydroxyguanidine tosylate-derived Schiff bases, compound 54 (Fig. 6) was shown to be very effective against mouse hepatitis virus (MHV), inhibiting its growth by 50% when employed at concentrations as low as 3.2 l M .

Schiff base linkage with pyridoxal 5' phosphate (PLP) a derivative of pyridoxine commonly known as vitamin B6 abolished the enzyme activities of Proteins. PLP binds to number of specific enzymes and play a critical role in helping these enzymes to catalyze their reaction. Most enzymes that interact with PLP catalyze reactions involved in the metabolism of amino acids. In many PLP dependent enzymatic reactions, PLP forms a Schiff base link with Lysine residue on the enzyme. Another Schiff Base complex of 2-pyridine carboxyaldehyde and its derivative show high super oxide dismutase activities [25]. Ternary complex of Cu(II) containing NSO donar Schiff base showed DNA Cleavage activities.

4. DNA Binding and Cleavage:

DNA is an important drug target and it regulates many biochemical processes that occur in the cellular system. Survey of literature demonstrates that interest in the design of novel transition metal complexes capable of binding and cleaving duplex DNA with high sequence and structure selectivity increases continuously. Additionally, the metal ion type and different functional groups of ligands, which are responsible for the geometry of complexes, also affect the affinity of metal complexes to DNA[26].

In addition, as small molecules, a great many Schiff-base complexes with transition metals have provoked wide interests because of their diverse biological and pharmaceutical activities**.**

The importance of certain compounds in medical diagnosis and genomic research is based on the ability of such compounds to bind and cleave double stranded DNA under physiological conditions. The hydrolytic and oxidative cleavage pathways are involved in DNA cleavage reactions. The formation of fragments may be considered to take place through enzymatic processes which occurs due to hydrolysis of phosphodiester. The nucleobase oxidation and/or degradation of sugar by abstraction of sugar hydrogen atoms take place during oxidative process. The oxidative cleavage of DNA is brought about by various methodologies and the methodology which involves irradiation with visible light of longer wavelength, has achieved significant importance for the major use in photodynamic therapy (PDT) of cancer. The DNA cleavage reaction is also considered of prime importance as it proceeds by targeting various constituents of DNA viz., the nucleic bases, deoxyribose sugar moiety and phosphodiester linkage**.**

The binding ability of DNA is the main source for making the comparison in cleavage efficiency of the complexes to that of the control. The open circular DNA is obtained from super coiled DNA by complexes. The account of DNA cleavage by hydroxyl radicals abstraction of a hydrogen atom from sugar units and proposed general mechanisms that predict the release of specific residues which arise from transformation of sugars, which also depends on the position of hydrogen atom removal. The hydroxyl radical mediated cleavage reactions and cleavage of peroxy derivatives is inhibited by free radical scavengers.

Investigations on the interactions of DNA with transition metal complexes provide leads for rational drug design, as well as means for the development of sensitive chemical probes for DNA[27].

These interactions would be either covalent or non-covalent. In covalent binding the labile part of the complex is replaced by a nitrogen base of DNA. On the other hand, the non-covalent DNA interactions include intercalative, electrostatic and groove binding of cationic metal complexes along periphery of the DNA helix, the major or minor groove. The different loci present in the DNA are involved in various regulatory processes such as gene expression, gene transcription, mutageneis, carcinogenesis, etc. Many small molecules exert their anticancer activities by binding with DNA, thereby altering DNA replication and inhibiting the growth of tumor cells. The DNA cleavage reaction is also considered of prime importance as it proceeds by targeting various constituents of DNA viz., the nucleic bases, deoxyribose sugar moiety and phosphodiester linkage. Intercalation involves the partial insertion of aromatic heterocyclic rings between the DNA base pairs.

5. Anticancer

It has been reported that chelation is the cause and cure of many diseases including cancer. Angiogenesis-dependent diseases are controlled by using chemotherapy, immunotherapy and radiation therapy to inhibit the stimulating or stimulate the inhibiting factors.

It is a complex process encompassing endothelial cell migration, proliferation and tube formation. These are well-regulated processes involving a number of stimulators.

Inhibition of angiogenesis is considered to be one of the promising strategies in the development of novel antineoplastic therapies. Complexes of cobalt (II), nickel (II) and copper(II) with potential biologically active Schiff base ligand, bis(3-acetylcoumarin) thiocarbohydrazone show cytotoxic activity[28].

6. Antioxidant Activity:

Free radicals contain one or more unpaired electrons, produced in normal or pathological cell metabolism. Reactive oxygen species (ROS) react easily with these free radicals to become radicals themselves. ROS are various forms of activated oxygen, which include free radicals such as superoxide anion radicals (O_2^-) and hydroxyl radicals (OH•), as well as non-free radical species (H_2O_2) and the singled oxygen .They are formed in living organisms in different ways, including normal aerobic respiration, stimulated polymorphonuclear leukocytes and macrophages, and peroxisomes[29].

The free radicals and reactive oxygen species (ROS) are involved in complete damage of our tissues and such type of damage can be avoided by employing antioxidants. The amount of ROS, which is removed, is detoxified by mitochondria and at the same time, ROS are generated at the mitochondrial site. The capacity of removal of ROS from mitochondria could be very much different from that of generated ROS. The difference in ROS removal and generation leads to the emission of ROS outside the mitochondria.

The rate of emission of ROS and the production of ROS by extra mitochondrial resources determines the steady state ROS concentration. The antioxidant properties of the Schiff base ligands were evaluated in a series of in vitro tests: 1, 1-diphenyl-2-picrylhydrazyl (DPPH) free radical scavenging and reducing power activity of superoxide anion radical generated non-enzymatic systems.

Conclusion

Schiff bases and their metal complexes are one of the most important chemical classes of compounds having a common integral feature of a variety structural diversity and of active medicinal agents. This review reflects the contribution of Schiff bases to the design and development of novel lead having potential biological activities. This bioactive core has maintained the interest of researchers in gaining the most suggestive and conclusive access in the field of various Schiff bases of medicinal importance from last decades. The present paper is an attempt to review the chemistry of Schiff bases and their metal complexes also their catalytic and Ribonucleotide Reductage activity.

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Conflict of interest

The authors have no conflict of interest to publish the article.

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