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Schiff base complexes as versatile pharmacophores of metallopharmaceutical interest-A review

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Abstract
This review is mainly focused on the biological significance of Schiff base complexes. Schiff bases and their metal complexes are fascinating ligands which are synthesized from the chemical reaction between a primary amine compound and carbonyl grouping. These compounds and their metal complexes are very important as pivots in various biological systems, polymers, dyes and medicinal and pharmaceutical fields. These compounds exhibit useful biological activities such anti-inflammatory, analgesic, antimicrobial, anticonvulsant, antitubercular, anticancer, antioxidant, anthelmintic, antiglycation, and antidepressant activities. These molecular scaffolds are also used as catalysts, pigments and dyes, intermediates in organic synthesis, polymer stabilizers, and corrosion inhibitors. Also, their use in birth control and food packages is outlined in this review.
Keywords: *Biological activities, Catalysts, Metal complexes, Schiff base, Antifungal,Polymers ect.*

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I. Introduction

Metal complexes play an essential role in agriculture, Pharmaceutical and industrial chemistry. Ligand, a metal surrounded by a cluster of ions or molecule, is used for preparation of complex compounds named as Schiff bases[1], which are condensation products of primary amines and aldehydes or ketones (RCH=NR$_i$, where R & R$_i$ represents alkyl and / or aryl substituents). Schiff base complexes are characterized by an excellent catalytic activity in a variety of reactions at high temperature (>100ºC) and in the presence of moisture. In recent years, there have been numerous reports of their use in homogeneous and heterogeneous catalysis.This paper reviews uses of Schiff bases and their metal complexes as catalysts, in various biological systems, polymers and dyes, besides some uses as antifertility and enzymatic agents. Due to the excellent stability of Schiff bases for specific metal ions such as Al(II), Co(III), Ag(II), Gd(II), Cu(III), Hg(II), Ni(II), Pb(II), Y(III) and Zn(II), a large number of different Schiff base ligands have been used as carriers in potentiometric sensors, due to catalytic properties of Schiff bases exhibit the catalytic activity in the hydrogenation of olefins. One of them more interesting applications of these compounds is the possibility to use them as effective corrosion inhibitors.

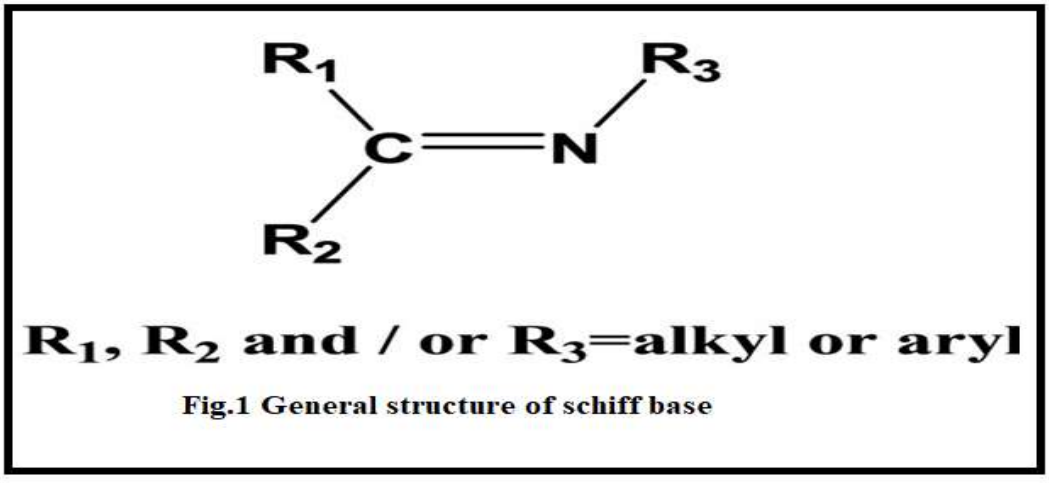
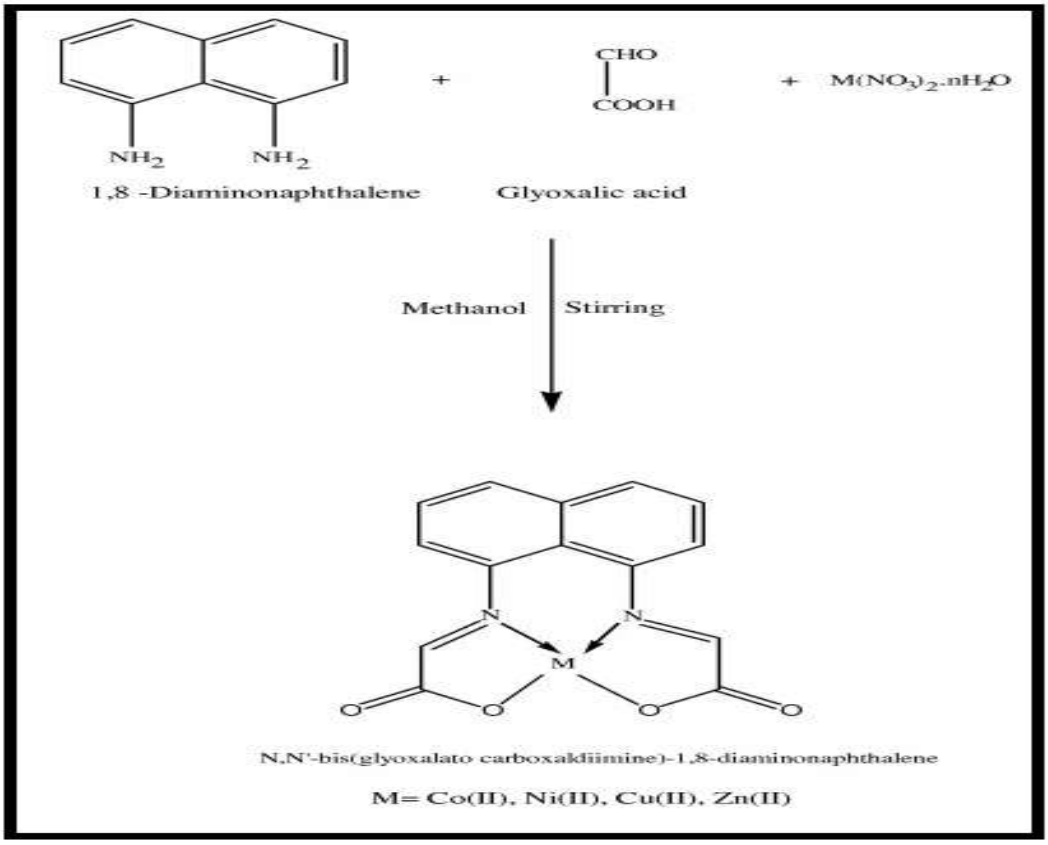


Fig.1 General structure of schiff base

Catalysts

Aromatic Schiff bases or their metal complexes catalyze reactions on oxygenation[2,3], hydrolysis[4], electro-reduction[5], and decomposition[6]. Four coordinated Co(II) Schiff base chelate complexes[2] show catalytic activity in oxygenation of alkene. Metalloporphyrins[3] oxidize phenols (naphthol). Some copper complexes, derived with amino acids, enhance (10-50 times) hydrolysis rate[4] more than simple copper (II) ion. Synthetic iron (II) Schiff base complex exhibits catalytic activity towards electro-reduction of oxygen[5]. Some metal complexes of a polymer bound Schiff base show catalytic activity on decomposition of hydrogen peroxide and oxidation of ascorbic acid[6]. Cyanohydrins cobaltate complexes exhibit catalytic activity[7]



Biological Activities

(i) Antimicrobial Activities:

Schiff base[8] derived from furylglyoxal and p-toluidene show antibacterial activity against Escherichia coli, Staphylococcus aureus, Bacillus subtilis, and Proteus vulgaris. Complexes of thallium (I) with benzothiazolines[9] show antibacterial activity against pathogenic bacteria. Various metal complexes in IInd and IVth oxidation state derived with aniline[10-14] show different behaviour with different types of bacteria. Metal complexes[15] of Mo (IV) and Mn (II) with ligands hydrazine carboxamide and hydrazine carbothiamide show antibacterial activity against S. aureus and Xanthomonas compestris. Tridentate Schiff bases[16-19] and their metal complexes show antibacterial activities against E. coli S. aureus, B. subtilis and B. pumpilis. Some aldimines[20] (E & Z forms), pyrazine[21], amino acid derived Schiff bases[22-24] and heterocylic-ketone derived Schiff bases[25,26] show antibacterial activity. Some heterocyclic Schiff bases[27-29] can act as a antibacterial agent. Isatin derived Schiff bases[30,31] possess anti-HIV activity and antibacterial activity. Schiff bases (benzimidazole[32], toluidinones[33], quin-azolinones[34], furaldehyde[35], thiazole[36, 37], pyridine[38] and benzyldithio -carbazate[39,40], glucosamine[41], pyrazolone [42,43], hydrazide [44], furfuraldiam-ine [45], halogenated [46], thiazolidiones or azetidiones[47], indole[48], p-fluorobenzaldehyde[49], p-anisidiene[50], thio-semi-carbazone[51], thiadiazo-lines[52] and imidazolinones[53]) show antibacterial activity. Schiff bases, ligands[54] containing cyclo-butane and thiazole rings, show antimicrobial activity. Schiff bases of pyrolidione, pyridone with o-phenylenediamine and their metal complexes[55] show antibacterial activity. N-5 chloro-salicylidiene tauriene Schiff base[56] and its Cu, Ni complexes show antibacterial activities to C*olibacillus* and *Pseudomonas aeruginosa.* Schiff base conjugates of p-amino salicylic acid[57] enhance antimyco-bacterium activity against *Mycobacterium smegmatis* and *M. lovis BCG*. Schiff base[58-60] with thiophene carboxaldehyde and aminobenzoic acid show antibacterial activity. Lysine

based Schiff bases and their complexes[61] with La, Co, Fe, show bacteriostatic activity to *B. subtilis, E. coli* and *S. aureus*. Zn (II), Cd (II), Ni (II) and Cu (II) complexes with furfural and semicarbazide[62], and with furfurylidene diamine[63] Schiff bases show antibacterial activities. Salicylidene derivatives[64], neutral tetra-dentate ligand and metal- complexes[65] show antibacterial activities against *S. typhi, S. aureus, Kelbsiella pneumoniae, B. subtlis* and *S. flexneri*. Organo-silicon (IV) complexes[66] with bi- dentate Schiff base, and organo-silicon (IV) complexes[67] and organo-lead (IV) complexes[68] with nitrogen donar ligands of sulpha drugs possess antibacterial activities. Using microcalorimetery[69], antibacterial activities against *E. coli* of Schiff bases and their metal complexes can be studied.

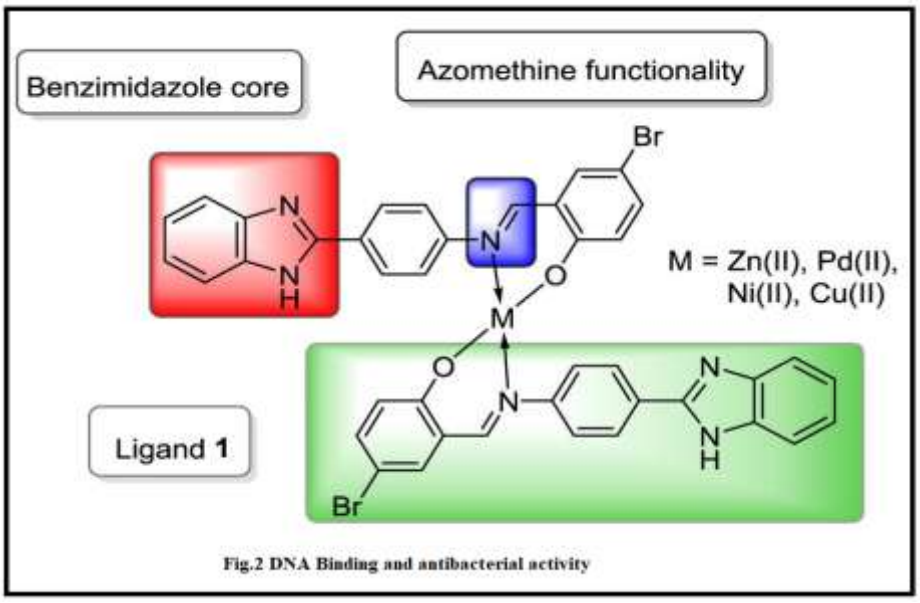


Fig.2 DNA Binding and antibacterial activity

(ii) Antifungal Activities:

Thiazole and benzothiazole Schiff bases[70] possess effective antifungal activity. Presence of methoxy, halogen and napthyl groups enhance fungicidal activity towards *Curvularia.* Pyrandione Schiff bases[71] show physiological activity against *A. niger.* Some Schiff bases of quinazolinones[72] show antifungal activity against *Candida albicans, Trichophyton rubrum, T. mentagrophytes, A. niger* and *Micosporum gypseum.* Furfurglidene nictoinamide Schiff base[73] shows antifungal activity against *A. niger, Alternaria solani* and *Collectotricum capsici.*Schiff bases and their metal complexes[74] formed between furan or furylglycoxal with various amines show antifungal activity against *Helminthosporium gramineum* (causing stripe disease in barely), *Syncephalostrum racemosus* (causing fruit rot in tomato) and *C. capsici* (causing die back disease in chillies). Moreover, ligand hydrazine and carbothioamide[75] and their metal complexes show antifungal activity against *A. alternata* and *H. graminicum.* Molybdenum and manganese complexes control disease (caused by *A.alternata*) in brinjal crop. Benzothiazole or phenyl-azo-thiazole[27] derived Schiff bases and metal complexes show microbiological activity against *A. niger* and *A. alternata.* Tridentate Schiff base[76] and their metal complexes show biocidal activites. Ruthenium (II) complexes[77] with Schiff base salicyladmine, thalium(I) complexes[78] with benzothiazolines, copper (II) complexes[79] of benzoylpyridine Schiff base show antifungal activities. Oxovanadium (IV) complexes[80] with triazole shows antifungal activity.As (III), Sb (III), and Bi (III) complexes[81] with o- tolylammonium di-thiocarbamate are antifungal against *A. niger* and *A. alternata*. Some novel cephalexin- derived Schiff bases[82] and their metal complexes show antifungal activities. Schiff bases[83] derived from salicylaldehydes and boronate esters show antifungal activities against *A. niger* and *A. flaves.* Schiff base[84] of salicylaldehyde and *O,O*-di-methyl thiophosphoramide and their complexes with Cu(II), Ni(II), and Zn(II) are effective chemicals to kill *Tetranychus bimaculatus.*

(iii) Antiviral Activities:

Schiff bases of gossypol[85] show high antiviral activity. Silver complexes[86] in oxidation state I showed inhibition against *Cucumber mosaic* virus; glycine salicylaldehyde Schiff base Ag (I) [86], gave effective results up to 74.7% towards *C. mosaic* virus.

Other Therapeutic Activities:

Several Schiff bases possess anti-inflammatory, allergic inhibitors reducing activity[96] radical scavenging[96], analgesic[97] and anti-oxidative action[98]. Thiazole derived Schiff bases[99] show analgesic and anti-inflammatory

activity. Schiff base of chitosan and carboxymethyl-chitosan shows an antioxidant activity such as superoxide and hydroxyl scavenging[100]. Furan semicarbazone metal complexes[101] exhibit significant anthelmintic and analgesic activites[101].

(iv) **Anti Tumor and Cytotoxic Activities:**

Salicylidiene anthranilic acid[102] possesses antiulcer activity and complexation behaviour with copper complexes, which show an increase in antiulcer activity. Some Schiff bases[103] and their metal complexes containing Cu, Ni, Zn and Co were synthesized from salicylaldehyde, 2,4 dihydroxy- benzaldehyde, glycine and L-alanine and possess antitumor activity and their order of reactivity with metal complexes is Ni>Cu>Zn>Co. Amino Schiff bases[104] derived with aromatic and heterocylic amine possess high activity against human tumor cell lines. Aryl-azo Schiff bases[105] exhibit anticancer activity. Schiff base of indole-2-caboxaldehydes[106] show inhibitor activities to K B cell lines. Diorgano- tin (IV) complexes and Schiff base[107] show antitumor activities *in vitro* and inhibit interaction to K B HCT-8 and BEL-7402 tumor cell lines.

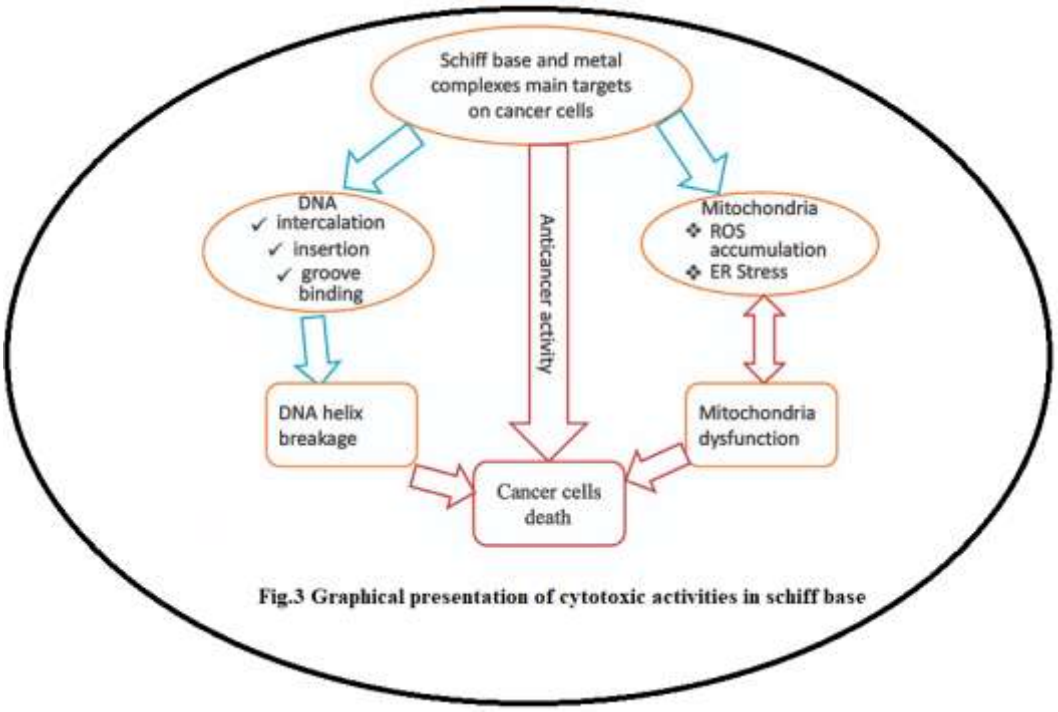


Fig.3 Graphical presentation of cytotoxic activities in schiff base

(v) Polymers:

Photochemical degradation of natural rubber yield amine[108] terminated liquid natural rubber (ATNR) when carried out in solution, in presence of ethylene- diammine. ATNR on reaction with glyoxal yield ploy Schiff base[108], which improves aging resistance. Organocobalt complexes with tridentate Schiff base act as initiator of emulsion polymerization and co- polymerization of dienyl and vinyl monomers[109].

(vi) Antifertility and Enzymatic Activity

Schiff bases[15] of hydrazine carboxoamide and hydrazine and metal complexes of dioxo Mo (IV) and Mn (II) might alter reproductive physiology. Schiff base[110] linkage with pyridoxal 5'phosphate from lysine to alanine or histidine abolishes enzyme activity in protein.

(vii) Miscellaneous Applications

Chemistry of amine induced, head separation and action by pyridoxal, indicate that head and tail of sperm are joined by Schiff base[119] formed between proteins within nuclear membrane. Effect of N-salicylaldehyde amino glucose (SG) Schiff base complex[120] with Cu (II) and Zn (II) inhibit synthesis of O_2 markedly; inhibitory effect of Cu (SG) was more than that of Zn (SG). Complexes Cu (SG) and Co (SG) combine with salman sperm DNA. Tetradentate Schiff base and its metal complexes with Mn (II), Ni (II), Cu (II), and Zn (II) show miscellaneous effect on membrane in amylose productions. Zn (II) and Mn (II) complexes stimulated amylose transportation through membrane while, Ni (II), and Cu (II) complexes inhibited it.Some Schiff bases[121] possess simple harmonic generation activity. Amido-Schiff base forms chelates with Cu (II) and Fe (II) and acts as a thrombin inhibitor[122]. Carnosine and anserine act as effective trans-glycating agent in decomposition of aldose-derived Schiff bases[123]

II. Conclusion

The review of literature discussed above is a gentle introduction towards Schiff bases in special attention to pharmaceutical interest. Depending upon the nature of condensation moieties (ketonic or aldehydic) with primary amine a large number of novel compounds are reported every year with applicability in various material science aspects. Under such purview Schiff base functional group can serve as an enhancer of bio-membrane traversing capability. In addition to various other catalytic aspects the type of disease to be encountered also matters. Nowadays, theoretical chemistry is applied before synthesizing a compound of this sort and fruitful results are first depicted and if found feasible, a suitable synthetic route is followed to synthesize Schiff base compounds.

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