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# Application of Schiff bases and their metal complexes-A Review

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**Abstract:** Schiff bases are versatile ligands which are synthesized from the condensation of an amino compound with carbonyl compounds. These compounds and their metal complexes are very important as catalysts in various biological systems, polymers, dyes and medicinal and pharmaceutical fields. Their use in birth control, food packages and as an $O_2$ detector is also outlined. This review summarizes the applications of Schiff bases and their complexes.
**Keywords:** Schiff bases, metal complexes, biological activity, nonlinear optical properties.

## Introduction

Schiff bases derived from an amino and carbonyl compound are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been studied extensively [1]. In azomethine derivatives, the C=N linkage is essential for biological activity, several azomethines were reported to possess remarkable antibacterial, antifungal, anticancer and diuretic activities [2]. Schiff bases have wide applications in food industry, dye industry, analytical chemistry, catalysis, fungicidal, agrochemical and biological activities[3].With the increasing incidence of deep mycosis, there has been increasing emphasis on the screening of new and more effective antimicrobial drugs with low toxicity. Schiff-base complexes are considered to be among the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety[4].A considerable number of Schiff-base complexes have potential biological interest, being used as more or less successful models of biological compounds [5]. Not only have they played a seminal role in the development of modern coordination chemistry, but also they can also be found at key points in the development of inorganic biochemistry, catalysis and optical materials [6].

## (1) Antimicrobial Activities

### Antibacterial Activities

Schiff base derived from indoline-2, 3-dione and 2-aminobenzoic acid and its Tin complex showed antibacterial activity against *Staphylococcus aureus*. The results compared with standard drug (Imipinem) have indicated that compounds were active but activity was lesser than the standard drug. This activity might be due to the presence of a hydroxyl and phenyl group [7]. The increased activity in the organotin complexes may be due to the coordination and polarity of a tin(IV) atom with oxygen of the ligand. The order of increasing activities is ligand < MeSnL < PhSnL < $BZ_3SnL$, the results matched with the previously

reported data for the biological activity of organotin complexes [8]. Complexes of Co(II),Cu(II),Ni(II),Mn(II) and Cr(III) with Schiff bases derived from 2,6-diacetylpyridine and 2-pyridine carboxaldehyde with 4-amino-2,3-dimethyl-1-phenyl-3-pyrozolin-5-one show antibacterial and antifungal activities against *Escherichia coli, Staphylococcus aureus, Klebsiella pneumoniae, Mycobacterium Smegmatis, Pseudomonas aeruginosa, Enterococcus cloacae, Bacillus megaterium* and *Micrococcus leteus*. The results showed that $L^1$ ligand has a greater effect against *E. coli* than the other bacteria while it has no activity against *S. aureus*. Metal complexes have a greater effect than $L^2$ against almost all bacteria [9]. The Schiff base 4-chloro-2-(2-morphiolinoethylimino) methylphenolato methanolchloro and its Zn(II) complex were screened for antibacterial activity against two Gram positive bacterial strains (*B. subtilis* and *S. aureus*) and two Gram-negative bacterial strains(*E. coli* and *P. fluorescence*) by the MTT method. The Schiff base showed significant activity against two Gram-negative bacterial strains with MIC of 12.5µgm$L^{-1}$but was inactive against two Gram negative bacterial strains. The Zn complex showed a wide range of bactericidal activities against the Gram positive and Gram negative bacteria, were potent than, or similar with commercial antibiotics (Kanamycin and penicillin) [10]. Bidentate complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with benzofuran-2-carbohydrazide and benzaldehyde [BPMC] or 3,4-dimethoxybenzalde hyde[BDMePMC] showed biological activities. Co(II) and Cd(II) complexes of [BPMC] are moderately active toward *E.coli* whereas Cu(II), Zn(II) and Ni(II) complexes of [BPMC] and Cu(II) and Zn(II) complexes of [BDMeOPMC] are more active against *S.aurious* as compared to free ligands. None of the complexes are active against *A.niger*, but in the case of *A.fumigatus*, Cu(II),Co(II), Ni(II) and Cd(II) complexes of [BDMeOPMC] are more active than the parent ligands[11]. Amino acid Schiff base derived from 2-hydroxy-5-methylacetophenone and glycine and its transition metal complexes showed bacterial activities. The ligand was bacteriostatic against bacterial strains except *Proteus vulgaris, Shigella flexneri*, and *Bacillus coagulans.* All complexes are either resistant or less sensitive against *P.vulgaris*. However compared to the antibacterial activity of the standard antibiotic streptomycin, the activity exhibited by the ligand and metal complexes was lower. The metal complexes showed to exhibited higher activity than the free ligand against the same organism under identical experimental conditions, such increased activity of the metal chelates can be explained on the basis of chelation theory[12]. Mixed ligand complexes with 2,6-pyridinecarboxaldehydebis(p-hydroxyphenylamine($L^1$), 2,6-pyridinecarbox - aldehydebis(o-hydroxyphenylamine($L^2$) showed anti - bacterial activities. The data obtained reflect that the two Schiff base ligands $L^1$ and $L^2$ have moderate activity in comparison with *Staphylococcus aureus, Escherichia coli* and less active in comparison with *Pseudomonas aeruginosa*. $L^1$ ligand shows a moderate activity towards *Bacillus subtilis* while $L^2$ ligand is less active. The remarkable activity of the two Schiff base ligands may be arise from the pyridyl-N and the hydroxyl groups which may play an important role in the antibacterial activity[13] as well as the presence of two imine groups which imports in elucidating the mechanism of transformation reaction in biological system[13]. Tetra and hexacoordinate metal chelate complexes of phosphate Schiff base ligands were found to be possess remarkable bacterial properties, it is however interesting that the biological activity gets enhanced on undergoing complexation with the metal ions[14]. Neutral tetradentate complexes of transition metals with Schiff bases derived from 2-aminophenol/2-aminothiophenol and 1-phenyl-2,3-dimethyl-4(4-iminopentan-2-one)-pyrazol-5-one showed antimicrobial activity against *Staphylococcus aureus, Bacillus subtilis, Klebsiella imeumoniae, Salmonella typhi, Pseudomonous aeruginosa, Shigella flexneri, Aspergillus niger* and *Trichoderma viridi*. Most of the complexes have higher activity than the free ligand[15]. Complexes of transition metal with Schiff base derived from 2,3-dihrdrazinoquinoxaline(DHQ) showed antimicrobial acyivity. Preliminary testing of the ligand and metal complexes for antimicrobial activity on the gram positive *S.aureus* and gram negative *E.coli* shows that the ligand is active only against *S.aureus* and the activity is enhanced by complexation. The metal complexes exhibit more bacreriostatic activity against *E.coli*. The appearance of activity may be due to synergistic mechanism[16]. A tridentate Schiff base derived from the condensation of S-benzyldithiocarbazate with salicyldehyde and transition metal complexes showed significant bioactivity against *Pseudomonas aeruginosa* (gram negative) and *Bacillus cereus* (gram positive) while the uranium analogue was effective against *Bacillus cereus* and showed very weak activity against *Candida albicans* fungi[17].

## Antifungal Activities

The microbial activity of the N-(2-hydroxy-1-naphthalidene)phenylglycine and its transition metal complexes was investigated. From the antifungal screening data it is concluded that the activity of the ligand has increased upon complexation. Cu(II), Ni(II)

and Co(II) complexes have shown better antifungal activity compared to the ligand and the corresponding metal salts[18]. Two bidentate Schiff base ligands 2-(2-hydroxy-3, 5-dichloro/dibromo) benzaldehyde-[4-(3-methyl-3-mesitylcyclobutyl)-1, 3-thiazol-2-yl]hydrazone, $L^1H$, $L^2H$ and their metal complexes were tested against a yeast-like fungus *C.albicans*[19]. The fungicidal effect of salicylaldimine containing formaldehyde and piperazine moity and its metal polychelates were determind against two yeast *Candida albicans, Aspergillus*. The Cu(II)-polychelate exhibited high activity against *Candida albicans* and the other show mild activity. The presence of N and O donor groups in the ligand and its metal polychelates inhibited enzyme production because enzymes that require free hydroxyl group for their activity appear to be especially susceptible to deactivation by the metal ion of polychelates. All the metal polychelates are more toxic than the ligand[20]. Neutral complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases derived from 3-nitrobenzylidene-4- aminoanttipyrine and aniline($L^1$)/p-nitroaniline($L^2$)/p-methoxyaniline ($L^3$) showed antifungal activity. A comparative study of the MIC values for the ligands and their complexes indicates that the complexes exhibit higher antimicrobial activity. Such increased activity of the complexes can be explained on the basis of overtone's concept and Tweedy's chelation theory[21]. Inhibition is enhanced with the introduction of an electron withdrawing nitro group in the phenyl ring[22]. Semicarbazones and thiosemicarbazones complexes of Ni(II) metal showed antifungal activities against 11 pathogenic fungi. The complexes were moderate active against all pathogenic fungi and much lower than those of standard fungicide Nistatin[23]. Co(II),Ni(II) and Cu(II) complexes with Schiff base 3,3'-thiodipropionic acid bis(4-amino-5-ethylimino-2,3-dimethyl-1-phenyl-3-pyrazoline showed antifungal activity against *Alternaria brassicae, Aspergillus niger* and *Fusarium oxysprum* and results indicate that the complexes show the enhanced activity in comparison to free ligand[24].

## Antitumor and Cytotoxic Activities

Metal complexes of Schiff base derived from 2-thiophenecarboxaldehyde and 2-aminobenzoic acid (HL) have been recommended and/ or established a new line for search to new antitumor particularly when one knows that many workers studied the possible antitumor action of many synthetic and semi synthetic compounds e.g. Hodnett et al. and Hickman[25]. Such compounds may have a possible antitumor effect since Gram-negative bacteria are considered a quantitative microbiological method testing beneficial and important drugs in both clinical and experimental tumor chemotherapy[26]. A tridentate Schiff base derived from the condensation of S-benzyldithiocarbazate with salicyldehyde and its Zn, Sb, Cu complexes showed cytotoxic properties[27]. Copper(II) complexes containing Schiff bases derived from S-benzyldthiocarbazate and saccharinate showed anticancer properties. The complexes were highly active against the leukemic cell line (HL-60) but only [Cu(NNS)(sac)] was found to exhibit strong cytotoxicity against the ovarian cancer cell line (Caov-3). The activities being higher than the standard anticancer drug Doxorubicin[28]. Compexes of chromium(III) are much less cytotoxic than chromium(VI) to cultured human cells[29]. Chromium(III) is an essential nutrient that is involved in the glucose tolerance factor(GTF) in maintenance of normal carbohydrate and lipid metabolism[30].

## Antiviral Activities

Schiff bases of gossypol show high antiviral activity[31]. Silver complexes in oxidation state I showed inhibition against Cucumber mosaic virus; glycine salicylaldehyde Schiff base Ag(I), gave effective results up to 74% towards C.mosaic virus[32].

## Synthetic Action on Insecticides

Schiff base derived from sulfane thiadizole and salicylaldehyde or thiophene-2-aldehydes and their complexes show toxicities against insects[33]. α-Aminoacid acts as intermediate in synthesis of photostable pyrthriod insecticides[34]. Flourination on aldehyde part of Schiff base enhances insecto acracicidal activity[35]. Schiff bases (thiadiazole derivatives with salicylaldehyde or o-vanillin) and their metal complexes with Mo(II) show insecticidal activities against bollworm and promote cell survival rate of mung bean sprouts[36].

## Plant Growth Regulator

N-acetylated compounds show growth inhibitory activity with seedling of wheat, rye and barley[37]. Schiff bases show remarkable activities on plant hormone such as the auxins on root growth[38]. Schiff base of ester and carboxylic acid show remarkable activity as plant growth hormone[39]. Schiff bases of thiodiazole have good plant growth regulator activity towards auxin and cytokine[40].

## Other Therapeutic Activities

Several Schiff bases possess anti – inflammatory, allergic inhibitors reducing activity radical scavenging, analgesic and anti-oxidative action[41]. Thiazole derived Schiff bases[42] show analgesic and anti-

inflammatory activity. Schiff base of chitosan and carboxymethyl-chitosan shows an antioxidant activity such as superoxide and hydroxyl scavenging. Furan semicarbzone metal complexes exhibit significant anthelmintic and analgesic activites[42].

## (2) Catalysts

Co(II), Fe(III) and Ru(III) complexes of Schiff bases derived from hydroxy benzaldehyde are used in oxidation of cyclohexane into cyclohexanol and cyclohexanone in presence of hydrogen peroxide. The most efficient catalysts are the Fe(III) complexes which is unusual because, in general, the cobalt(II) complexes have high activity for alkane oxidation reactions[43]. Chromium-salen complexes are well-known catalysts both in heterogeneous and homogeneous[44]. Binucleating complexes of Fe, Co, Ni, Zn with Schiff bases neytralbis(iminopyridyl)benzene and monoanionic bis(iminopyridyl)phenolate acts as catalysts in the oligomerisation of ethylene[45]. New manganese(II) and manganese(III) complexes of substituted N,N'-bis(salicylidine)-1,2-diimino-2-methylene appear to be efficient models for peroxidase activity[46]. New Copper(II) complexes of indoxyl thiosemicarbazone (ITSC) show one pair of well defined reduction peaks at different potential in the forward scan, which represent the reduction of $Cu^{++}$ to $Cu^{+}$ by one electron process and subsequent oxidation of $Cu^{+}$. The quasi-reversible nature of the $Cu^{++}/Cu^{+}$ is due to inherent reducing tendency of thiosemicarbazone ligands[47]. Ruthenium and cobalt complexes with Schiff bases bis-salicylaldehyde-o-phenylene-diaimine(saloph) and substituted(Cl,Br and $NO_2$) oxidize α-pinene into camphene, 2,7,7-trimethyl ss pinene(3-oxatricyclo-4,1,1,o2,4-octane), 2,3-epoxy, campholene aldehyde and D-verbenone[48]. Ni(II) complexes with bidentate(NN) ligands become an efficient catalyst precursor for olefin oligomerisation in presence of an activator[49]. A wide variety of cobalt(II) complexes are known to bind dioxygen more or less reversibly and are therefore frequently studied as model compounds for natural oxygen carrier and for their use in $O_2$ storage, as well as in organic syntheses due to their catalytic properties under mild conditions[50].

## (3) Antifertility and Enzymatic Activity

About 20 Zinc enzymes are known in which Zinc is generally tetrahedrally four coordinate and bonded to hard donor atoms such as nitrogen or oxygen[51]. The Schiff base complexes of 2-pyridinecarboxaldehyde and its derivatives have been reported to posses high super oxide dismutase activities[52]. Recently, the interaction of DNA with complexes [Cr(Schiff base)$(OH_2)_2$]$ClO_4$ was reported[53]. Ternary complexes of Cu(II) containing NSO donor Schiff base showed DNA cleavage activity. In the presence of 3-mercaptopropionic acid (5mM) as a reducing agent, the complexes (40 μM) show efficient DNA cleavage activity giving the order NSO-dppz > ONO-dppz > NSO-dpq > ONO dpq[54].

## (4) Dyes

Chromium azomethine complexes, cobalt complex Schiff base[55], unsymmetrical complex 1:2 chromium[56] dyes give fast colours to leathers, food packages, wools etc. Azo groups containing metal complexes[57] are used for dying cellulose polyester textiles. Some metal complexes are used to mass dye polyfibers[58]. Cobalt complex[59] of a Schiff base (salicylaldehyde with diamine) has excellent light resistance and storage ability and does not degrade even in acidic gases ($CO_2$). Novel tetradentate Schiff base acts as a chromogenic reagent for determination of Ni in some natural food samples[60].

## (5) Polymer

Photochemical degradation of natural rubber yield amine terminated liquid natural rubber(ATNR) when carried out in solution, in presence of ethylenediamine[60]. ATNR on reaction with glyoxal yield poly Schiff base[60], which improves aging resistance. Organocobalt complexes with tridentate Schiff base act as initiator of emulsion polymerization and co-polymerization of dienyl and vinyl monomers[61].

## (6) Miscellaneous Applications

Transition metal complexes with 1, 10-phenanthroline and 2, 2-bipyridine are used in petroleum refining[62]. Popova and Berova reported that copper is good for liver function, its level in blood and urine has influence in pregnancy disorders, nephritis hepatitis, leprosy, anemia and leukemia in children[63]. NLO Metal complexes of Schiff base derived from tetradentate precursor 1-phenylbutane-1, 3-dionemono S-methylisothiosemicarbazone with o-hydroxy benzaldehyde or its phenylazoderivative showed nonlinear optical (NLO) properties. A comparison between complexes of different metals with the same phenylazo-substituted ligand indicated that the NLO response strongly depends upon the electronic configuration of the metal center[64]. It has been reported that Zinc(II) complexes with Schiff bases type chelating ligands can be used as an effective emitting layer[65]. In addition, it has also been shown that Zinc(II) complexes with benzothiazoles, which are

oxidized forms of benzothiazolines are luminescent[66]. Zinc(II) and Cadmium(II) complexes with $N_2S_2$ -Schiff base ligands are a new class of luminescent compounds, and the careful derivatization of the substituents on the pendent phenyl rings permits a finetuning of the emission wavelength[67]. Baker's yeast contains a benzofuran derivative which acts as an antioxidant preventing haemorrhagine liver necrosis in rats and haemolysis of red cells in vitamin E deficiency[68]. Amino acid Schiff base complexes derived from 2-hydroxy-1-naphthaldehydes are important due to their use as radiotracers in nuclear medicine[69]. Macrocyclic Schiff bases of Dithiocarbazic acid have many fundamental biological functions, such as photosynthesis and transport of oxygen in mammalian and other respiratory system[70].

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