

Applications of metal complexes of Schiff bases-A review

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Applications of Schiff bases and their metal complexes as catalysts, in various biological systems, polymers and dyes are described. Their use in birth control, food packages and as an O₂ detector is also outlined.

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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 bases¹, which are condensation products of primary amines and aldehydes or ketones (RCH=NR', where R & R' represents alkyl and / or aryl substituents). 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.

Catalysts

Aromatic Schiff bases or their metal complexes catalyze reactions on oxygenation^{2,3}, hydrolysis⁴, electro-reduction⁵, and decomposition⁶. Four coordinated Co(II) Schiff base chelate complexes² show catalytic activity in oxygenation of alkene. Metalloporphyrins³ oxidize phenols (naphthol). Some copper complexes, derived with amino acids, enhance (10-50 times) hydrolysis rate⁴ more than simple copper (II) ion. Synthetic iron (II) Schiff base complex exhibits catalytic activity towards electro-reduction of oxygen⁵. Some metal complexes of a polymer bound Schiff base show catalytic activity on decomposition of hydrogen peroxide and oxidation of ascorbic acid⁶. Cyanohydrins cobaltate complexes exhibit catalytic activity⁷.

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Biological Activities

Antimicrobial Activities

Schiff base⁸ derived from furylglyoxal and p-toluidene show antibacterial activity against Escherichia coli, Staphylococcus aureus, Bacillus subtilis, and Proteus vulgaris. Complexes of thallium (I) with benzothiazolines⁹ show antibacterial activity against pathogenic bacteria. Various metal complexes in IInd and IVth oxidation state derived with aniline¹⁰⁻¹⁴ show different behaviour with different types of bacteria. Metal complexes¹⁵ of Mo (IV) and Mn (II) with ligands hydrazine carboxamide and hydrazine carbothiamide show antibacterial activity against S. aureus and Xanthomonas compestris. Tridentate Schiff bases¹⁶⁻¹⁹ and their metal complexes show antibacterial activities against E. coli S. aureus, B. subtilis and B. pumpilis. Some aldimines²⁰ (E & Z forms), pyrazine²¹, amino acid derived Schiff bases²²⁻²⁴ and heterocyclic-ketone derived Schiff bases^{25,26} show antibacterial activity. Some heterocyclic Schiff bases²⁷⁻²⁹ can act as a antibacterial agent. Isatin derived Schiff bases^{30,31} possess anti-HIV activity and antibacterial activity. Schiff bases (benzimidazole³², toluidinones³³, quin-azolinones³⁴, furaldehyde³⁵, thiazole^{36,37}, pyridine³⁸ and benzyldithio -carbazate^{39,40}, glucosamine⁴¹, pyrazolone^{42,43}, hydrazide⁴⁴, furfuraldiam-ine⁴⁵, halogenated⁴⁶, thiazolidiones or azetidiones⁴⁷, indole⁴⁸, p-fluorobenzaldehyde⁴⁹, p-anisidiene⁵⁰, thio-semi-carbazone⁵¹, thiadiazolines⁵² and imidazolinones⁵³) show antibacterial activity. Schiff

bases, ligands⁵⁴ containing cyclo-butane and thiazole rings, show antimicrobial activity.

Schiff bases of pyrrolidione, pyridone with o-phenylenediamine and their metal complexes⁵⁵ show antibacterial activity. N-5 chloro-salicylidene taurine Schiff base⁵⁶ and its Cu, Ni complexes show antibacterial activities to *Colibacillus* and *Pseudomonas aeruginosa*. Schiff base conjugates of p-amino salicylic acid⁵⁷ enhance antimyco-bacterium activity against *Mycobacterium smegmatis* and *M. lovis BCG*. Schiff base⁵⁸⁻⁶⁰ with thiophene carboxaldehyde and aminobenzoic acid show antibacterial activity. Lysine based Schiff bases and their complexes⁶¹ 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 semicarbazide⁶², and with furfurylidene diamine⁶³ Schiff bases show antibacterial activities. Salicylidene derivatives⁶⁴, neutral tetra-dentate ligand and metal-complexes⁶⁵ show antibacterial activities against *S. typhi*, *S. aureus*, *Kelbsiella pneumoniae*, *B. subtilis* and *S. flexneri*. Organo-silicon (IV) complexes⁶⁶ with bi-dentate Schiff base, and organo-silicon (IV) complexes⁶⁷ and organo-lead (IV) complexes⁶⁸ with nitrogen donor ligands of sulphur drugs possess antibacterial activities. Using microcalorimetry⁶⁹, antibacterial activities against *E. coli* of Schiff bases and their metal complexes can be studied.

Antifungal Activities

Thiazole and benzothiazole Schiff bases⁷⁰ possess effective antifungal activity. Presence of methoxy, halogen and naphthyl groups enhance fungicidal activity towards *Curvularia*. Pyrandione Schiff bases⁷¹ show physiological activity against *A. niger*. Some Schiff bases of quinazolinones⁷² show antifungal activity against *Candida albicans*, *Trichophyton rubrum*, *T. mentagrophytes*, *A. niger* and *Micosporum gypseum*. Furfurylidene nictoinamide Schiff base⁷³ shows antifungal activity against *A. niger*, *Alternaria solani* and *Collectotricum capsici*.

Schiff bases and their metal complexes⁷⁴ formed between furan or furyl glyoxal with various amines show antifungal activity against *Helminthosporium gramineum* (causing stripe disease in barely), *Syncephalostrium racemosus* (causing fruit rot in tomato) and *C. capsici* (causing die back disease in chillies). Moreover, ligand hydrazine and carbathioamide⁷⁵ 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-thiazole²⁷ derived Schiff bases and metal complexes show microbiological activity against *A. niger* and *A. alternata*. Tridentate Schiff base⁷⁶ and their metal complexes show biocidal activities. Ruthenium (II) complexes⁷⁷ with Schiff base salicylaldimine, thalium(I) complexes⁷⁸ with benzothiazolines, copper (II) complexes⁷⁹ of benzoylpyridine Schiff base show antifungal activities. Oxovanadium (IV) complexes⁸⁰ with triazole shows antifungal activity.

As (III), Sb (III), and Bi (III) complexes⁸¹ with o- tolylammonium di-thiocarbamate are antifungal against *A. niger* and *A. alternata*. Some novel cephalixin- derived Schiff bases⁸² and their metal complexes show antifungal activities. Schiff bases⁸³ derived from salicylaldehydes and boronate esters show antifungal activities against *A. niger* and *A. flavus*. Schiff base⁸⁴ of salicylaldehyde and *O,O*-di-methyl thiophosphoramidate and their complexes with Cu(II), Ni(II), and Zn(II) are effective chemicals to kill *Tetranychus bimaculatus*.

Antiviral Activities

Schiff bases of gossypol⁸⁵ show high antiviral activity. Silver complexes⁸⁶ 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*.

Synergistic Action on Insecticides

Schiff base⁸⁷ derived from sulfane thiazole and salicylaldehyde or thiophene-2-aldehydes and their complexes show toxicities against insects. α -Amino acid⁸⁸ acts as intermediate in synthesis of photostable pyrthriod insecticides. Flourination⁸⁹ on aldehyde part of Schiff base enhances insecto-acaricidal activity. Schiff bases (thiadiazole derivatives with salicylaldehyde or o-vanillin) and their metal complexes⁹⁰ with Mo (IV) show insecticidal activities against bollworm and promote cell survival rate of mung bean sprouts.

Plant Growth Regulator

N-acetylated compounds⁹¹ show growth inhibitory activity with seedling of wheat, rye and barley. Schiff bases^{92,93} show remarkable activities on plant hormone such as the auxins on root growth. Schiff base⁹⁴ of ester and carboxylic acid show remarkable activity as plant

growth hormone. Schiff bases of thiodiazole have good plant growth regulator activity towards auxin and cytokin⁹⁵.

Other Therapeutic Activities

Several Schiff bases possess anti-inflammatory, allergic inhibitors reducing activity⁹⁶ radical scavenging⁹⁶, analgesic⁹⁷ and anti-oxidative action⁹⁸. Thiazole derived Schiff bases⁹⁹ show analgesic and antiinflammatory activity. Schiff base of chitosan and carboxymethyl-chitosan shows an antioxidant activity such as superoxide and hydroxyl scavenging¹⁰⁰. Furan semicarbazone metal complexes¹⁰¹ exhibit significant anthelmintic and analgesic activities¹⁰¹.

Anti Tumor and Cytotoxic Activities

Salicylidene anthranilic acid¹⁰² possesses antiulcer activity and complexation behaviour with copper complexes, which show an increase in antiulcer activity. Some Schiff bases¹⁰³ 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 bases¹⁰⁴ derived with aromatic and heterocyclic amine possess high activity against human tumor cell lines. Aryl-azo Schiff bases¹⁰⁵ exhibit anticancer activity. Schiff base of indole-2-carboxaldehydes¹⁰⁶ show inhibitor activities to K B cell lines. Diorganotin (IV) complexes and Schiff base¹⁰⁷ show antitumor activities *in vitro* and inhibit interaction to K B HCT-8 and BEL-7402 tumor cell lines.

Polymers

Photochemical degradation of natural rubber yield amine¹⁰⁸ terminated liquid natural rubber (ATNR) when carried out in solution, in presence of ethylenediamine. ATNR on reaction with glyoxal yield poly Schiff base¹⁰⁸, which improves aging resistance. Organocobalt complexes with tridentate Schiff base act as initiator of emulsion polymerization and copolymerization of diene and vinyl monomers¹⁰⁹.

Antifertility and Enzymatic Activity

Schiff bases¹⁵ of hydrazine carboxamide and hydrazine and metal complexes of dioxo Mo (IV) and Mn (II) might alter reproductive physiology. Schiff base¹¹⁰ linkage with pyridoxal 5'phosphate from lysine to alanine or histidine abolishes enzyme activity in protein.

Dyes

Chromium azomethine complexes¹¹¹, cobalt complex Schiff base¹¹², un-symmetrical complex 1:2 chromium^{113,114} dyes give fast colours to leathers, food packages, wools etc. Azo groups containing metal complexes^{115,116} are used for dyeing cellulose polyester textiles. Some metal complexes¹¹⁷ are used to mass dye polyfibers. Cobalt complex¹¹² of a Schiff base (salicylaldehyde with diamine) has excellent light resistance and storage ability and does not degrade even in acidic gases (CO₂). Novel tetradentate Schiff base acts as a chromogenic reagent for determination of Ni in some natural food samples¹¹⁸.

Miscellaneous Applications

Chemistry of amine induced, head separation and action by pyridoxal, indicate that head and tail of sperm are joined by Schiff base¹¹⁹ formed between proteins within nuclear membrane. Effect of N-salicylaldehyde amino glucose (SG) Schiff base complex¹²⁰ with Cu (II) and Zn (II) inhibit synthesis of O₂ markedly; inhibitory effect of Cu (SG) was more than that of Zn (SG). Complexes Cu (SG) and Co (SG) combine with salmon 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 bases¹²¹ possess simple harmonic generation activity. Amido-Schiff base forms chelates with Cu (II) and Fe (II) and acts as a thrombin inhibitor¹²². Carnosine and anserine act as effective trans-glycating agent in decomposition of aldose-derived Schiff bases¹²³.

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