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Schiff Base Ligand System and their Applications in Biological System, Catalysis and in Chemosensing: A Short Review

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ABSTRACT:
Schiff base are the versatile ligands, prepared by the condensation reaction of primary amines with carbonyl compounds. Schiff base along their metal complexes having numerous application in catalysis, medicinal chemistry, polymerization, chemosensing and in organic compound synthesis. Due to broad spectrum of catalytic activities, Schiff base metal complexes are very useful in epoxidation, oxidation, reduction of ketones, and in polymerization. Their biological activity includes antibacterial, antifungal, antimicrobial, anticancer, antimalarial and antiviral etc. In this review we present the use of Schiff base and their metal complexes in catalysis, biological and in chemosensing activities.

Introduction

Schiff base ligands are the condensation product of primary amines and carbonyl compounds. They were first synthesized by Hugo Schiff in 1864. These are represented by $R_1N=CR_2R_3$ where R_1, R_2 and R_3 may be alkyl or aryl groups. They were first reported by Hugo Schiff in 1864 [1], so these are named after him. They are formed according to the following reaction scheme 1.

$$\underset{\text{Amine}}{R_1NH_2} + \underset{\text{Ketone or aldehyde}}{R_2C(=O)R_3} \longrightarrow \underset{\text{Schiff base}}{R_1N=CR_2R_3} + H_2O$$

Scheme 1. General scheme for Schiff base synthesis (where R_1, R_2 and R_3 may be an alkyl or aryl group.

Schiff bases containing aryl substituents can be synthesized easily and are more stable because of effective conjugation, while those containing alkyl substituents are relatively less stable than Schiff bases of aromatic aldehydes [2]. Due to stearic hindrance, ketones reacts slower than aldehydes. The azomethine group, N=CH- present in the Schiff base is responsible for reactivity, stability and biological activity of the metal complex. Schiff base ligand contains donor atom like Nitrogen and Oxygen, which provides the binding sites for metal ions through non-bonding electrons [3]. Schiff base along their metal complexes have good chelating property so these have numerous application in catalysis, polymerization, oxidation and in biological system.

Biological activity

Schiff bases contains an imine group –N=CH-, which helps to understand the mechanism of transamination and racemization reactions in biological system. Schiff bases exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, anticancer, anti-inflammatory, antiviral properties [4]. Metal complexes of Mn(II) with ligand hydrazine carbothiamide show antibacterial activity against xanthomonas compestris. Schiff base of pyrolidione, pyridine with o-phenylenediamine and their metal complexes show antibacterial activity [5]. Salicylidene derivatives [6,7] neutral tetradentate ligands show remarkable antibacterial activity against S. flexneri and K. pneumonia. Other Schiff base derivatives possess antibacterial activity are: thiazole, pyridine, pyrazolone, hydrazide and indole etc.

Recently there was a considerable increase in life threatening incidence of fungal infections [8], so development of some effective antifungal agents has

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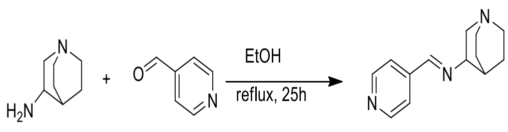
become the necessity, hence Schiff base and their metal complexes are considered to be promising antifungal medicines [9]. Benzothiazole Schiff base [10] shows effective antifungal activity. The presence of napthyl groups increases fungicidal activity toward Curvularia. Moreover some Schiff bases [11] like pyrandione and furfurglidene nictoinamide shows antifungal activities against alternariasolani and candida albicans. Ru(II) complex of salicyladmine and Cu(II) complex of benzoylpyridine show antifungal activity. Kumar *et al* [12] reported a series of 3-(benzylideneamino)-2-phenylquinazoline-4(3H)-one and evaluated their cytotoxicity and antiviral activity.

Schiff bases of gossypol [13] show high anti-viral activity. Compounds containing 2-hydroxy substitution showed even better anti-viral activity. Salicylaldehyde Schiff bases derived from 1-amino-3-hydroxyguanidine tosylate are promising material for development of new anti-viral agents.

Schiff bases are very interesting compounds which possess antimalarial properties due to interesting moiety for designing of antimalarial agents. Cryptolepine an alkaloid, isolated from African plant Cryptolepissanguinolenta is also used in the treatment of malaria,is a product of reaction in which Schiff base is involved [14]. Salicylidieneanthranlic acid show antiulcer activity.

Among the biocidal properties, bases of isatin derivatives are also used in the destruction of protozoa and other parasites. Schiff bases also possess antitumor activity. Imine derivatives of N-hydroxy-N'-aminoguanidine are used in the treatment of cancer [15].

Rupanjali Sharma and others [16] synthesized Schiff base ligand (SB 1) N-(pyridine-4yl-methylene) quinuclidine-3-amine derived from 3-amino-quinuclidine and 4-pyridine carboxaldehyde scheme 2. This synthesized Schiff base was found to exhibits antimalarial activity against chloroquine-sensitive plasmodium falciparum strain.



Scheme 2**.** Synthesis of Schiff base ligand 1 possessing antimalarial activity

Zn(II) complexes of Schiff base ligand obtained from condensation reaction of salicylaldehyde with 2-amino-4-phenyl-5-methyl thiazole have been studied for its anticancer activity against different human tumor cell line such as liver cancer HepG2, lung carcinoma A549 and breast cancer MCF-7.The studies revealed that Zn(II) complex exhibit significant inhibition against these cell lines as compared to inhibition in the untreated cells [17].

A new Schiff base ligand obtained from condensation reaction of diacetylmonoxime with benzidiene along with its Co(III) complex 1 in Figure 1 have been reported to show antibacterial activity against Bacillius Subtilis, however no activity was observed against gram – negative bacteria E. Faecalis and E. Coli [18]

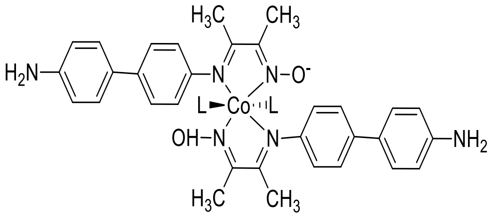


Figure 1. Structure of Schiff base Co(III) complex 1

Similarly Saidul and others [19] synthesized Schiff base ligands (SB 2) derived from the condensation of o-hydroxybenzaldehyde with amino phenol and form metal complexes with Co(II), Ni(II) and Cu(II) ions in Figure 2. These complexes show significant antifungal activities against Gram positive and gram-negative bacteria.

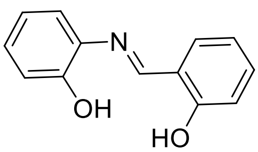


Figure 2. Schiff base ligand 2 possessing antifungal activity.

Schiff base ligand (SB 3) with three donor sites derived from 3-ethoxy salicylaldehyde and 2-amino benzoic acid was synthesized in Figure 3. The antibacterial and

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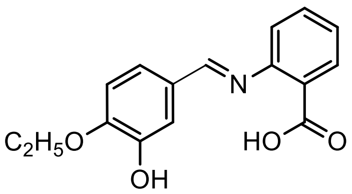
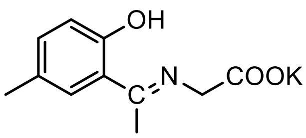
antifungal activities were explored by disc diffusion method. It was found that metal complexes of this tridentate ligand (Co(II), Ni(II), Zn(II) and Cu(II)) showed better antibacterial property as compare to Schiff base ligand [20].



SB 3

Figure 3. Structure of Schiff base ligand 3

Schiff base molecules (SB 4) in Figure 4 of amino acids like glycine as their potassium salts with 2-hydroxy- 5-methyl acetophenone and their complexes with divalent iron, nickel, zinc and manganese ions were prepared [21]. The ligand was trident with ONO donor sites except Zn(II), where it was monobasic bidentate.

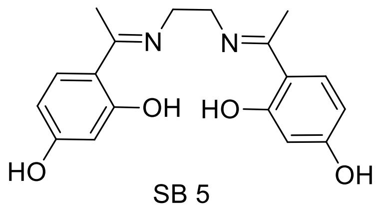


SB 4

Figure 4. Structure of amino acids Schiff base ligand 4

The antibacterial action of prepared ligand and their metal complexes against various gram-positive and gram-negative bacterial strains were studied *in-vitro* using Single Disc method. *Streptomycin* was taken as the standard antibiotic and DMSO as negative control. Incubation of plates were done for 24 hrs at 37°C. It was found that ligand and the metal complexes exhibited good antibacterial activity against bacterial strains except S.flexneri, B. coagulans and P. vulgaris. The antibacterial activity of ligand and metal complexes was found to be lower than standard antibiotic Streptomycin, however metal complexes showed better activity as compare to ligand.

Another example of tetradentate Schiff base ligand (SB 5) in Figure 5, which is prepared by refluxing a mixture of ethanolic solution of 1-2 ethanediamine and 4-acetylresorcinol [22]. Furthermore, their metal complexes have been reported which are synthesized by refluxing Schiff base ligand and metal acetates of metal ions such as Co(II) and Cu(II) and Ni(II) ions, respectively.

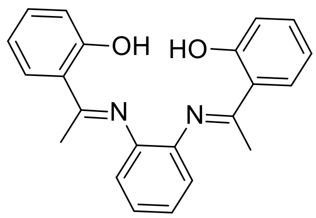


SB 5

Figure 5. Structure of Schiff base ligand 5

Antimicrobial activities of Schiff base ligand and their metal complexes were tested by Agar diffusion method for five bacteria strains against gram positive bacteria: B. cerus, S. faecalis, S. aureus and E. Coli, P. aeruginosa and gram-negative bacteria. The studies showed that metal complexes exhibit greater antibacterial activity as compared to their free ligand.

Some tetradentate ligand (SB 6) with N_2O_2 donor sites in Figure 6 and its complexes with Co(II) and Cu(II) metal ions were synthesized by the same strategies as discussed above [23]. Schiff base ligand along its Co(II) and Cu(II) complexes were tested for their antibacterial activity against the bacterial strain: E. Coli and B. cereus, S.aureus.



SB 6

Figure 6. Structure of Schiff base ligand 6

It was observed that Schiff base metal complexes show greater antibacterial potency against bacteria strain as compared to free Schiff base ligand.

Catalytic activity

Catalytic activities of Schiff base metal complexes are found in literature. These show high catalytic activity and played a important role in numerous reaction to enhance their yield and product selectivity. Their simple methods of synthesis along their thermal stability contribute significantly the possibility of their application in catalysis [24]. Schiff base along with

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their metal complexes are effective catalyst both in homogenous and heterogeneous reactions. Till date, they have been used for catalyzing various organic reactions like C-C bond formation, cross-coupling reactions, oxidation-reduction reactions etc. The catalytic activity of Schiff base and their metal complexes have been reported in various reactions.

Recently three Schiff base ligands (SB 7, 8 and 9) in Figure 7 have been derived from condensation reaction of 3-methoxy-2-hydroxybenzaldehyde and diamines 1, 2-diphenylendiamine, 1, 2-diamine-2-methylpropane and 1, 3-propanediamine [25]. Their manganese complexes were also tested as peroxidase mimics for H_2O_2 mediated reaction with the water trap ABTS. The studies show relevant peroxidase activity in complex of Schiff base 7 and 8 as compared to 9.

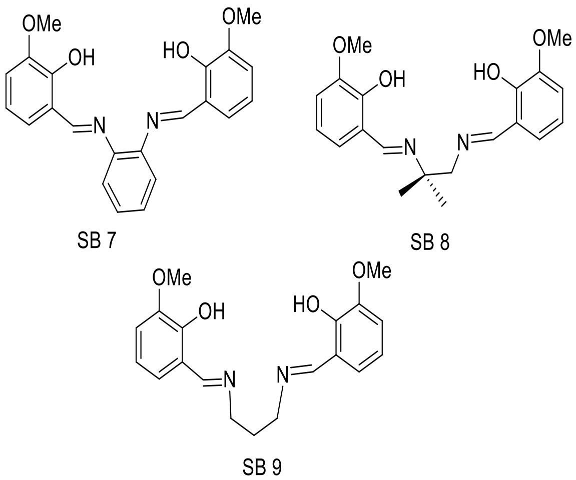
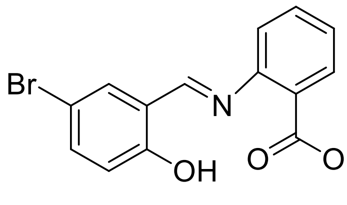


Figure 7. Structure of Schiff base ligands (7-9)

New Schiff base ligand (SB 10) containing ONO donor atoms in Figure 8 along with its Co(II), Cu(II) and Ni(II) complexes have been prepared from anthranilic acid and 5-bromosalicylaldehyde were used to check their catalytic activities [26].

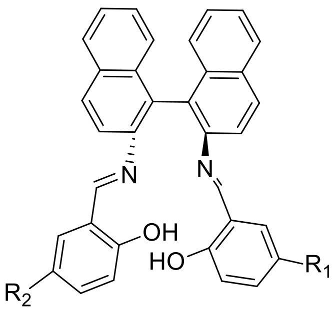


SB 10

Figure 8. Structure of Schiff base ligand 10

The catalytic study of redox reactions reveals that all metal complexes were found to increase the reaction rate of potassium persulphate and hydrogen peroxide with KI, further Ni(II) and Cu(II) complexes also exhibited a significant catalytic activity for benzopinacol formation reaction.

In the era of epoxidation reaction, The chiral Schiff base ligands (SB 11) in Figure 9 along with their Mn(II) complex have been reported to possess catalytic properties. The metal complexes were tested for their catalytic activity for the asymmetric epoxidation of styrene [27].



	R_1	R_2
L_1	H	OCH_3
L_2	H	OCF_3

SB 11, 12

Figure 9. Structure of chiral Schiff base ligands with ONNO donor sites

It was found that under similar experimental conditions epoxidation reaction with ditertiary butyl peroxide yields higher conversion and enantio-excess than the reaction with hydrogen peroxide. Furthermore the complex containing OCF_3 groups show much better results than the complex containing OCH_3 group in styrene oxide conversions.

Recently Co(II) complex of Schiif base ligands bis-5-phenylazosalicylaldehyde ethyldiamine and bis-5-phenylazosalicylaldehyde-o-phenylene diimine have been reported [28]. The synthesized Co(II) complexes were tested for their catalytic oxidation of styrene into methyl ketones in presence of oxygen and pyridine. The study reveals that selectivity of Co(II) complex of bis-5-phenylazosalicylaldehyde-o-phenylene diimine was found to be high in propanol and further increased with increasing amount of catalyst, however selectivity of

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Co(II) complex of bis-5-phenylazosalicylaldehyde ethyldiamine decrease with increase in concentration of catalyst.

Similarly asymmetric bidentate Schiff base ligand have been synthesized by condensation reaction of salicylaldehyde and tert-butyl amine [29], which was further used to form Zn(II), Co(II), Cu(II) and Pd(II) metal complexes. The reported metal complexes were used to check their catalytic activity for the selective oxidation of sulfides with H_2O_2 oxidant. The results shows that Zn(II) complex exhibited higher catalytic activity for oxidation of sulfides to the corresponding sulfones as compared to other metal complexes.

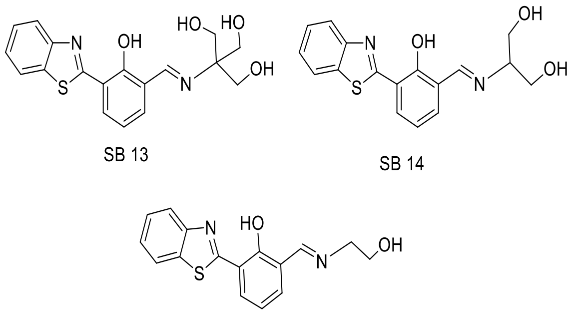
Schiff base as chemosensors

Schiff bases having high thermal stability, therefore they can be used as stationary phases in chromatography [30]. The determination methods of metals in different oxidation state mainly needs sophisticated instruments such as capillary electrophoresis, flame atomic absorption spectroscopy and inductively coupled plasma–atomic emission spectroscopy, which may not always convenient due to their high operational cost, maintenance expenses, needs expertise to run the instrument, complicated and laborious sample preparation. So due to simple monitoring and less expensive methods, chemosensor have gained importance in many disciplines such as biomedical and environmental sciences [31-33]

Schiff bases have coordinating sites which can capture metal ions and impart colors with some specific metal ions; hence they are used to sense some particular ions by naked eyes. In the past Schiff base moieties are used for designing highly selective and sensitive chemosensors for the detection of metal ions in aqueous and non aqueous medium. Amongst different chemosensors, chromogenic sensors have been important over the other recognition methods for detection of metal ions due to their sensitivity and selectivity to detect very low concentration without expensive instrumentation. Hence a cost effective chemosensor with high affinity for metal capturing should be designed.

Chemosensing based on colorimetric response and absorption/emission spectroscopic recognition is efficient, quick and cost effective offering detection limits comparable to the above mentioned techniques. Generally this technique require a chromophoric chelator which possesses donor sites for interacting metallic species and display a signal upon recognizing a particular metallic species.

Some benzothiazole-based Schiff base ligands (13-15) in Figure 10 acts as chemosensors for the recognition of Zn^{2+} ions have been reported [34], which give fluorescent turn-on signal with Zn^{2+} ions. The Schiff base chemosensors (13-15) showed different fluorescent emission upon binding with Zn^{2+} ions, which was absent in the presence of other metal ions. The studies revealed that chemosensor 13 was found to be highly sensitive toward Zn^{2+} ions in comparison of chemosensors 14 and 15, furthermore chemosensor 13 possess high cell permeability along with specific recognition of Zn^{2+} ions in living HeLa cells.

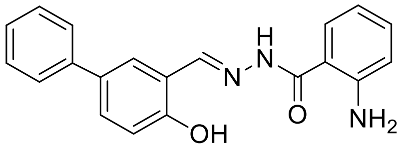


SB 13 SB 14

SB 15

Figure 10. Structure of Schiff base ligands (13-15) as chemosensors.

Another Schiff base ligand (16) in Figure 11 have have been reported [35], synthesized by condensation reaction of 5-phenyl salicylaldehyde and 2-aminobenzohydrizide and was used as chemosensor for recognition of Zn^{2+} ions in aqueous solution. The results show that upon addition of Zn^{2+} ions in aqueous solution of chemosensor, an intense green fluorescence emission with a significant red shift was observed, however no fluorescence was observed with other ions.



SB 16

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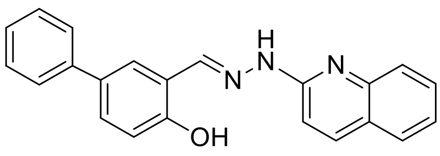
Figure 11. Structure of Schiff base ligand 16

Furthermore Schiff base chemosensor gives real-time monitoring of Zn^{2+} ions in biological system with minimal cell damage.

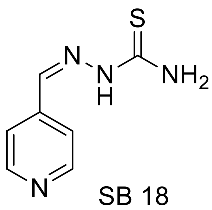
Recently a quinoline-based Schiff base ligand (17) in Figure 12 have been synthesized by condensation reaction of 2-hydroxy-1-naphthalene carboxaldehyde with 2-hydrazinoquinolone behave as chemosensor [36]. The colorimetric studies showed a rapid color change from colorless to yellow-orange upon addition of Cd^{2+} ion in Acetonitrile-water solution, however poor fluorescence emission was observed upon addition of Cd^{2+} ions, which was absent in presence of other ions.



SB 17

Figure 12. Structure of Schiff base ligand 17

Another new Schiff base ligand (18) in Figure 13 acts as chemosensor have been reported [37]. The reported chemosensor was explored for the selective recognition of Ag^{+} ions. The results shows that there is significant enhancement in fluorescence emission intensity upon addition of Ag^{+} ions, however no such effect was observed with other competing metal ions. Furthermore a chromogenic response was observed with Cu^{2+} ions.

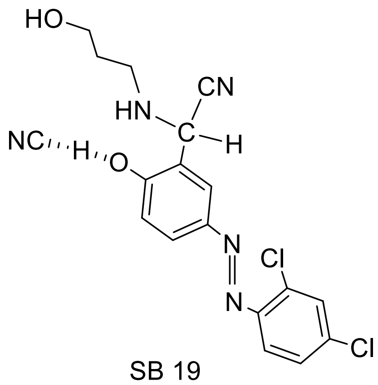


SB 18

Figure 13. Structure of Schiff base ligand 18

Similarly another chemosensor have been synthesized by condensation reaction of 1-pyrenecarboxaldehyde with 3-hydroxy-2-napthoic hydrazide [38]. The reported chemosensor was used as efficient fluorescent chemosensor for the recognition of Cu^{2+} ions which shows a gradual increase in fluorescence intensity upon addition of Cu^{2+} ions in DMSO:H_2O. In addition to this the reported chemosensor was used in the recognition of Cu^{2+} in biological system.

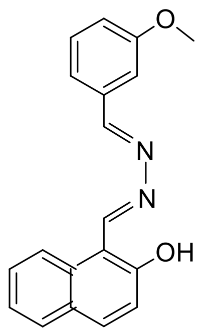
S.Amani and coworker [39] reported a new azo-azomethine colorimetric and optical chemosensor (19) 4-((2,4-dichlorophenyl)diaznyl-2-(3-hydroxypropylimino)methyl phenol in Figure 14. This receptor showed very selective colorimetric response to CN^{-} ion by changing its color from yellow to red dish orange in aqueous medium significantly this chemosensor can be used for detection of CN^{-} ion in basic conditions.



SB 19

Figure 14. Structure of Schiff base ligand 19

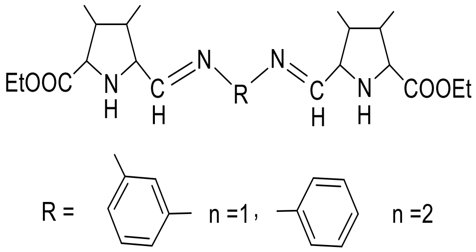
M.Shyamal and other synthesized fluorogenic sensor (20), 1-(2- hydroxyl napthylmethylene) -2-(3-methoxy -2-hydroxy benzylidienes)hydrazine in Figure 15. It exhibits excellent selectivity and rapid response toward Zn^{2+} based on CHEF/ AIEE features. The Schiff base receptor, not only can sense Zn^{2+} ion through sharp colorimetric and turn-on fluroscese response, but also can distinguish between its significant AIEE activity and Zn^{2+} triggered AIEE activity through individual emission signal [40].



SB 20

Figure 15. Structure of Schiff base ligand 20

Similarly P.Dong and coworker have synthesized a Schiff base chemosensor 1,3 and 1,4-bis(3,4-dimethyl -5-ethoxy–carbonyl pyrol-2-yl-methyleneamine) benzene (21. 22) in Figure 16. It exhibits high selectivity as off-on fluorescence sensor toward Zn^{2+} ion. It can sense Zn^{2+} by naked eye with color change from colorless to yellow and yellow to dark yellow [41].



SB 21, 22

Figure 16. Structure of Schiff base ligand 21 and 22

Conclusion

Due to their simple method of synthesis, Schiff base ligands and their metal complexes have been widely explored for their numerous applications in a variety of fields. In this review, the discussion has been focused on their biological, catalytic, and chemosensing properties. Schiff base ligands are highly versatile and have a wide range of applications, including their use as chemo/biosensors for the detection of metal ions and small molecules. These ligands offer advantages such as ease of synthesis, tunable properties, and potential for selective and sensitive detection, making them valuable tools in various disciplines.

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